TABLE OF CONTENTS

12th INTERNATIONAL CERAMICS CONGRESS

Symposium CA - CERAMIC POWDERS: SYNTHESIS, PROCESSING AND SINTERING

Oral Presentations

Symposium CB - NOVEL ROUTES FOR CERAMIC SYNTHESIS AND PROCESSING

Oral Presentations

Focused Session CB-11 - SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF CERAMICS

Oral Presentations

Focused Session CB-12 - LAYERED AND FUNCTIONALLY GRADED MATERIALS

Oral Presentations

Symposium CC - SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF CERAMICS

Oral Presentations

Symposium CD - CERAMIC JOINING

Oral Presentations

Symposium CE - CERAMICS AND COMPOSITES IN EXTREME ENVIRONMENTS

Oral Presentations

Symposium CF - CERAMICS FOR CHEMICAL, ELECTROCHEMICAL AND ENVIRONMENTAL APPLICATIONS

Oral Presentations

Session CF-3 - Catalysts and Catalysts Supports

Session CF-4 - Materials for Electrochemistry and Electrochemical Energy Conversion and Storage

Symposium CG - CERAMIC THIN FILMS AND COATINGS FOR PROTECTIVE, TRIBOLOGICAL AND MULTIFUNCTIONAL APPLICATIONS

Oral Presentations

Symposium CH - ADVANCES IN ELECTRICAL, MAGNETIC AND OPTICAL CERAMICS

Oral Presentations

Focused Session CH-6 - MULTIFERROICS

Oral Presentations

Symposium CI - MAGNETIC AND TRANSPORT PROPERTIES OF OXIDES

Oral Presentations

Symposium CJ - SCIENCE AND TECHNOLOGY FOR SILICATE CERAMICS

Oral Presentations

Symposium CK - GEOPOLYMERS AND GEOCEMENTS: LOW ENVIRONMENTAL IMPACT CERAMIC MATERIALS

Oral Presentations

Symposium CL - REFRACTORIES: RECENT DEVELOPMENTS IN MATERIALS, PRODUCTION AND USE

Oral Presentations

CM - 2nd International Conference
DISCLOSING MATERIALS AT NANOSCALE

Oral Presentations

CN - 6th International Conference
ADVANCED INORGANIC FIBRE COMPOSITES FOR STRUCTURAL AND THERMAL MANAGEMENT APPLICATIONS

Oral Presentations

Chair

Pietro Vincenzini
World Academy of Ceramics

Co-Chair

Akio Makishima
International Ceramic Federation

Advisory Boards

SYMPOSIUM CA - Ceramic Powders: Synthesis, Processing and Sintering

Programme Chair: Jean François Baumard, *France* *Members:* Mufit Akinc, *USA* Lennart Bergstrom, *Sweden* Stuart Blackburn, *UK* Aldo R. Boccaccini, *Germany* Paul Bowen, *Switzerland* Francis J. Cambier, *Belgium* W. Roger Cannon, *USA* C. Barry Carter, *USA* I-Wei Chen, *USA* Hans-Eckart Exner, *Germany* Gideon Grader, *Israel* Krzysztof Haberko, *Poland* Stuart Hampshire, *Ireland* Juergen G. Heinrich, *Germany* Yoshihiro Hirata, *Japan* Junichi Hojo, *Japan* Hae Jin Hwang, *Korea* Frank Kern, *Germany* Doh-Yeon Kim, *Korea* Mikito Kitayama, *Japan* Sridhar Komarneni, *USA* Fred Lange, *USA* Romano Lapasin, *Italy* Rodrigo Moreno, *Spain* Eugene A. Olevsky, *USA* Momcilo M. Ristic, *Serbia* Jürgen Rödel, *Germany* Andreas Roosen, *Germany* Yoshio Sakka, *Japan* Saburo Sano, *Japan* C.C. Sorrell, *Australia* Satoshi Tanaka, *Japan* Veena Tikare, *USA* Jose Arana Varela, *Brazil* Koji Watari, *Japan* Guo-Jun Zhang, *China*

SYMPOSIUM CB - Novel Routes for Ceramics Synthesis and Processing

Programme Chair: Ralf Riedel, *Germany* *Members:* Dinesh K. Agrawal, *USA* David Avnir, *Israel* Florence Babonneau, *France* Joachim Bill, *Germany* J.P.G. Binner, *UK* Christian Bonhomme, *France* Raj Bordia, *USA* Jin-Ho Choy, *Korea* Mark M. De Guire, *USA* Etienne Duguet, *France* Mohan Edirisinghe, *UK* Nahum Frage, *Israel* Takashi Goto, *Japan* Peter Greil, *Germany* Keijiro Hiraga, *Japan* Nicola Huesing, *Germany* Hubert Huppertz, *Austria* Leonard V. Interrante, *USA* Edwin Kroke, *Germany* Terence G. Langdon, *USA* Ya-Li Li, *China* Yoshitake Masuda, *Japan* Gary Messing, *USA* Philippe Miele, *France* Kazuki Nakanishi, *Japan* Takeshi Okutani, *Japan* Clément Sanchez, *France* Tsugio Sato, *Japan* Toshimori Sekine, *Japan* Yoshiyuki Sugahara, *Japan* Yoko Suyama, *Japan* Naresh N. Thadhani, *USA* Omer Van Der Biest, *Belgium* Monika Willert-Porada, *Germany* Masahiro Yoshimura, *Japan*

Focused Session CB-11 - Self-propagating High-temperature Synthesis of Ceramics

Chair: Alexander G. Merzhanov, *Russia* *Coordinator:* Hamazasp E. Grigoryan, *Russia* *Members:* Frédéric Bernard, *France* Inna P. Borovinskaya, *Russia* Giacomo Cao, *Italy* Elazar Gutmanas, *Israel* Suren Kharatyan, *Armenia* Evgeny Levashov, *Russia* Jerzy Lis, *Poland* Alexander Mukasyan, *USA* Zuhair A. Munir, *USA* Manshi Ohyanagi, *Japan* Roman Pampuch, *Poland* Alexander E. Sytschev, *Russia* Galina Xanthopoulou, *Greece*

Focused Session CB-12 - Layered and Functionally Graded Materials

Chair: Changchun GE, *P.R. China* *Members:* Serkan Dag, *Turkey* Moshe P. Dariel, *Israel* Martin Friess, *Germany* Michael M. Gasik, *Finland* Jae-Ho Jeon, *Korea* Akira Kawasaki, *Japan* Jeong-Ho Kim, *USA* Kiyotaka Matsuura, *Japan* Luis Augusto Rocha, *Portugal* Alexander S. Rogachev, *Russia*

SYMPOSIUM CC - Progress in the Understanding and Control of Ceramics Surfaces for Tribology and Corrosion

Programme Chair: Mark Hadfield, *UK* *Members:* Koshi Adachi, *Japan* Yasuhisa Ando, *Japan* Christopher Dellacorte, *USA* Jay Fineberg, *Israel* Mike Graham, *Canada* Richard H.J. Hannink, *Australia* Kiyoshi Hirao, *Japan* Masami Ikeyama, *Japan* Lars-Gunnar Johansson, *Sweden* Thomas Klassen, *Germany* Tapio Mantyla, *Finland* Denis Mazuyer, *France* Ronald A. Mccauley, *USA* James D. Mcguffin-Cawley, *USA* Kouji Miura, *Japan* Klaus G. Nickel, *Germany* Nobuo Ohmae, *Japan* Andreas A. Polycarpou, *USA* W. Mark Rainforth, *UK* W. Gregory Sawyer, *USA* James L. Smialek, *USA* Mineo Suzuki, *Japan* Karl-Heinz Zum Gahr, *Germany*

SYMPOSIUM CD - Ceramic Joining

Programme Chair: Alberto Passerone, Italy *Members:* Mathieu Brochu, *Canada* Robin A.L. Drew, *Canada* Christian Elsaesser, *Germany* Nikos Eustathopoulos, *France* John A. Fernie, *UK* Natalya

Froumin, *Israel* Masahiro Fukumoto, *Japan* Andreas Glaeser, *USA* Mark Hoffman, *Australia* Wayne Kaplan, *Israel* Kevin M. Knowles, *UK* Charles Lewinsohn, *USA* Y. Naidich, *Ukraine* Kiyoshi Nogi, *Japan* Ivar E. Reimanis, *USA* Manfred Roth, *Switzerland* Natalia Sobczak, *Poland* Tadatomo Suga, *Japan* Katsuaki Suganuma, *Japan* Shun-Ichiro Tanaka, *Japan* Antoni P. Tomsia, *USA*

SYMPOSIUM CE - Ceramics and Composites in Extreme Environments

Programme Chair: Sheldon Wiederhorn, Nist, *USA* *Members:* Fritz Aldinger, *Germany* Narottam P. Bansal, *USA* Michel Barsoum, *USA* Theodore M. Besmann, *USA* Philippe Colomban, *France* Robert Danzer, *Austria* Goffredo De Portu, *Italy* Jan Dusza, *Slovakia* William A. Ellingson, *USA* Gilbert Fantozzi, *France* Adrian Goldstein, *Israel* Georg Grathwohl, *Germany* Greg Hilmas, *USA* Michael J. Hoffmann, *Germany* Karl Jakus, *USA* Sylvia Johnson, *USA* Katsutoshi Komeya, *Japan* Edgar Lara-Curzio, *USA* Laura Montanaro, *Italy* Mats Nygren, *Sweden* Giuseppe Pezzotti, *Japan* Abel Rousset, *France* Pavol Sajgalík, *Slovakia* Gerold Schneider, *Germany* Vincenzo M. Sglavo, *Italy* Vladimir Ja Shevchenko, *Russia* Rolf Steinbrech, *Germany* Tierry Tiegs, *USA* Wei-Hsing Tuan, *Taiwan* Fumihiro Wakai, *Japan* Yanchun Zhou, *China*

SYMPOSIUM CF - Ceramics for Chemical, Electrochemical and Environmental Applications

Programme Chair: Paolo Colombo, *Italy* *Members:* Sheikh A. Akbar, *USA* Florence Ansart, *France* Mario Aparicio, *Spain* Alan Atkinson, *UK* Juana Benavente Herrera, *Spain* Henny J.M. Bouwmeester, *The Netherlands* Carlo Cantalini, *Italy* M.D. De Mello Innocentini, *Brazil* Sylvain Deville, *France* Scott W. Donne, *Australia* Jose L.G. Fierro, *Spain* Ludwig Gauckler, *Switzerland* Tatsumi Ishihara, *Japan* Saiful Islam, *UK* Ellen Ivers-Tiffee, *Germany* Yuji Iwamoto, *Japan* Nitin Labhsetwar, *India* Jan Luyten, *Belgium* Alessandro Martucci, *Italy* Kazushige Ohno, *Japan* Alain Pierre, *France* Aleksander Pyzik, *USA* Armin Reller, *Germany* Yoshihiko Sadaoka, *Japan* Michael Scheffler, *Germany* Richard Sisson, *USA* Fabio Spizzo, *Italy* Jeffry W. Stevenson, *USA* Henk Verweij, *USA* Anil V. Virkar, *USA* Ulrich Vogt, *Switzerland* Toshiya Watanabe, *Japan* Anthony R. West, *UK* Sujanto Widjaja, *USA* Wojtek Wlodarski, *Australia* Atsuo Yamada, *Japan* Jinhua Ye, *Japan*

SYMPOSIUM CG - Ceramic Thin Films and Coatings for Protective, Tribological and Multifunctional Applications

Programme Chair: Ghislain Montavon, *France* *Members:* Sergey E. Alexandrov, *Russia* Samir Aouadi, *USA* Christoper C. Berndt, *Australia* Maher I. Boulos, *Canada* Raymond (Reuven) Boxman, *Israel* Viorel T. Braic, *Romania* Yip-Wah Chung, *USA* W.J. Clegg, *UK* Diederik Depla, *Belgium* Dongfeng Diao *China* Izhak Etsion, *Israel* Martin Fenker, *Germany* Steven L. Girshick, *USA* Wayne L. Gladfelter, *USA* Gregory Goh, *Singapore* Vladimir Gorokhovsky, *USA* Philippe Goudeau, *France* Papken Hovsepian, *UK* Ulf Jansson, *Sweden* Kwang-Ho Kim, *South Korea* Yoshinori Koga, *Japan* Seiji Kuroda, *Japan* Nadhira Laidani, *Italy* Erich Lugscheider, *Germany* Christian Mitterer, *Austria* Christian Moreau, *Canada* Javad Mostaghimi, *Canada* Chris Muratore, *USA* Daniel Nelias, *France* Paolo M. Ossi, *Italy* Nitin P. Padture, *USA* Joerg Patscheider, *Switzerland* Sophoclis Patsias, *UK* Rosendo Sanjines, *Switzerland* Naruo Sasaki, *Japan* Jochen M. Schneider, *Germany* Uwe Schulz, *Germany* Fuh-Sheng Shieu, *Taiwan* Dmitry V. Shtansky, *Russia* José Filipe Vilela Vaz, *Portugal* Bogdan G. Wendler, *Poland* Ping Xiao, *UK* Xian Ting Zeng, *Singapore* Sam Zhang, *Singapore*

SYMPOSIUM CH - Advances in Electrical, Magnetic and Optical Ceramics

Programme Chair: Vojislav V. Mitic, *Serbia* *Members:* Jun Akedo, *Japan* Neil Alford, *UK* Wolfgang Benecke, *Germany* Amar Bhalla, *USA* Guozhong Cao, *USA* Xiang Ming Chen, *China* Jose Maria De Teresa, *Spain* Brahim Elouadi, *France* Mohammed Es-Souni, *Germany* Albert Figueras, *Spain* Robert Freer, *UK* Daniel Guyomar, *France* Hajime Haneda, *Japan* Heli Jantunen, *Finland* Peter Kazansky, *UK* Eung Soo Kim, *Korea* Toshio Kimura, *Japan* Hermann Kohlstedt, *Germany* Makoto Kuwabara, *Japan* Alexander A. Lebedev, *Russia* Yongxiang Li, *China* Longtu Li, *China* Bill Milne, *UK* Sahn Nahm, *Korea* Toshio Ogawa, *Japan* Maria Lorena Pardo Mata, *Spain* David A. Payne, *USA* Gary R. Pickrell, *USA* Shashank Priya, *USA* Jianrong Qiu, *China* Vito Raineri, *Italy* Ramamoorthy Ramesh, *USA* Ahmad Safari, *USA* Nava Setter, *Switzerland* Yuichi Shimakawa, *Japan* Derek C. Sinclair, *UK* Arthur W. Sleight, *USA* Mas Subramanian, *USA* Danilo Suvorov, *Slovenia* Philippe Tailhades, *France* Yuri D. Tretyakov, *Russia* Susan Trolier-Mckinstry, *USA* Hong Wang, *China* Zuo-Guang Ye, *Canada* Ki Hyun Yoon, *Korea* Weiguang Zhu, *Singapore*

Focused Session CH-6 - Multiferroics

Chair: Alois Loidl, *Germany* *Members:* Agnes Barthelemy, *France* Mirza I. Bichurin, *Russia* Mark Blamire, *UK* Long-Qing Chen, *USA* Sang-Wook Cheong, *USA* Manfred Fiebig, *Germany* Michael Karkut, *France* Michel Kenzelmann, *Switzerland* Andrei L. Kholkin, *Portugal* Ce-Wen Nan, *China* Beatriz Noheda, *The Netherlands* Masanori Okuyama, *Japan* Ernie Pan, *USA* Juan-Manuel Perez-Mato, *Spain* J.F. Scott, *UK* Gopalan Srinivasan, *USA* Pam A. Thomas, *UK* Yoshinori Tokura, *Japan* Dwight Viehland, *USA*

SYMPOSIUM CI - Magnetic and Transport Properties of Oxides

Programme Chair: Dino Fiorani, *Italy* *Members:* Emilio Bellingeri, *Italy* Ami Berkowitz, *USA* Maurizio Ferretti, *Italy* Josep Fontcuberta, *Spain* Atsushi Fujimori, *Japan* Tomoji Kawai, *Japan* Tsuyoshi Kimura, *Japan* Hideomi Koinuma, *Japan* David Look, *USA* Fabio Miletto Granozio, *Italy* Liliana Mitoseriu, *Romania* Takashi Mizokawa, *Japan* Isabelle Monot-Laffez, *France* Satishchandra B. Ogale, *India* Giorgio Piccaluga, *Italy* Bernard Raveau, *France* Naurang L. Saini, *Italy* D.S. Schmool, *Portugal* Jean-Marc Triscone, *Switzerland* David Vanderbilt, *USA* Yonggang Zhao, *P.R. China*

SYMPOSIUM CJ - Science and Technology for Silicate Ceramics

Programme Chair: Michele Dondi, *Italy* *Members:* Magdi F. Abadir, *Egypt* Nitin V. Afzulpurkar, *Thailand* George N. Angelopoulos, *Greece* Giovanni Baldi, *Italy* Philippe Blanchart, *France* Anselmo O. Boschi, *Brazil* Richard Bowman, *Australia* William M. Carty, *USA* Kausik Dana, *India* Swapan Kumar Das, *India* Vilma Ducman, *Slovenia* B. Eftekhari Yekta, *Iran* Juan Carlos Factorovich, *Argentina* Dachamir Hotza, *Brazil* Leena Hupa, *Finland* Philip R. Jackson, *UK* Alpagut Kara, *Turkey* Ferhat Kara, *Turkey* Vladimir Kozhukharov, *Bulgaria* Joao A. Labrincha, *Portugal* Hongjie Luo, *China* Tiziano Manfredini, *Italy* Guillermo Monros, *Spain* Arnaldo Moreno Berto, *Spain* Redouane Moussa, *Morocco* Manuel Ocana Jurado, *Spain* Thierry Poirier, *Venezuela* Johannes H. Potgieter, *South Africa* Juan Jacobo Ruiz Valdes, *Mexico* Toyohiko Sugiyama, *Japan* Petra Sulcova, *Czech Republic* Giorgio Timellini, *Italy* Jacques Tirlocq, *Belgium* Paolo Zannini, *Italy* Jian Er Zhou, *China*

SYMPOSIUM CK - Geopolymers and Geocements: Low Environmental Impact Ceramic Materials

Programme Chair: Cristina Leonelli, *Italy* *Members:* Erez Allouche, *USA* Mirko Braga, *Italy* Christopher Cheeseman, *UK* Gui Demortier, *Belgium* Katja Dombrowski, *Germany* Constantino Fernandez Pereira, *Spain* Dechang Jia, *P.R. China* Waltraud M. Kriven, *USA* Zongjin Li, *P.R. China* Kenneth J.D. Mackenzie, *New Zealand* Alejandro Manzano Ramirez, *Mexico* Henk Nugteren, *Netherlands* Hassane Oudadesse, *France* Christos G. Papakonstantinou, *USA* Dan S. Perera, *Australia* Vijaya B. Rangan, *Australia* Kwesi Sagoe-Crentsil, *Australia* Frantisek Skvara, *Czekia* Pavel Straka, *Czekia* Bob Talling, *Finland* Amandio Teixeira Pinto, *Portugal* Benjamin Varela, *USA* Marcel Weil, *Germany* Frank Winnefeld, *Switzerland* Yunsheng Zhang, *P.R. China*

SYMPOSIUM CL - Refractories: Recent Developments in Materials, Production and Use

Programme Chair: James P. Bennett, *USA* *Members:* Esteban F. Aglietti, *Argentina* Charles Alt, *USA* Christos G. Aneziris, *Germany* Carmen Baudin, *Spain* Paulo R.H.M. Bittencourt, *Brazil* Michel Boussuge, *France* Richard C. Bradt, *USA* Elena Brandaleze, *Argentina* Thierry Cutard, *France* Axel Eschner, *Germany* Geraldo E. Goncalves, *Brazil* Delia Gutierrez-Campos, *Venezuela* Harald Harmuth, *Austria* William L. Headrick, *USA* Marc Huger, *France* Boris L. Krasny, *Russia* W.E. Lee, *UK* Valery V. Martynenko, *Ukraine* Josè Luis Mendoza Bedolla, *Mexico* Kusuhiro Mukai, *Japan* George Oprea, *Canada* Toshitaka Ota, *Japan* Victor Carlos Pandolfelli, *Brazil* Christopher Parr, *France* Jacques Poirier, *France* Peter Quirmbach, *Germany* Michael Rigaud, *Canada* Mototsugu Sakai, *Japan* Kwang Bo Shim, *Korea* Nigel Stone, *Australia* Kiyoshi Sugita, *Japan* Analia G. Tomba Martinez, *Argentina* Thorsten Tonnesen, *Germany* Patrick Wollants, *Belgium*

CM - *2nd International Conference* "Disclosing Materials at Nanoscale"

Co-Chairs: Christoph Gerber, *Switzerland* Yury Gogotsi, *USA* Koichi Niihara, *Japan* *Programme Chair:* Maurizio Ferrari, *Italy* *Members:* James H. Adair, *USA* Rui M. Almeida, *Portugal* Masakazu Aono, *Japan* Katsuhiko Ariga, *Japan* Yoshio Bando, *Japan* François Beguin, *France* Dieter Bimberg, *Germany* Richard J. Blaikie, *New Zealand* Brigitte Boulard, *France* Jürgen Brugger, *Switzerland* Enric Canadell, *Spain* R.P.H. Chang, *USA* Yong-Ho Choa, *Korea* Gan-Moog Chow, *Singapore* M. Lucia Curri, *Italy* Chunhai Fan, *China* Shoushan Fan, *China* Daisuke Fujita, *Japan* Lian Gao, *China* Malcolm L.H. Green, *UK* Martin P. Harmer, *USA* M. Saif Islam, *USA* Jing-Feng Li, *China* Marian Marciniak, *Poland* Meyya Meyyappan, *USA* Paolo Milani, *Italy* Seizo Morita, *Japan* Ungyu Paik, *Korea* David Pettifor, *UK* Alexander Quandt, *Germany* C.N.R. Rao, *India* Giancarlo C. Righini, *Italy* Albert Romano-Rodriguez, *Spain* Tohru Sekino, *Japan* Zhigang Shuai, *China* Richard W. Siegel, *USA* Xiaowei Sun, *Singapore* Masasuke Takata, *Japan* Setsuhisa Tanabe, *Japan* Zhong Lin Wang, *USA* Andrew T.S. Wee, *Singapore*

CN - *6th International Conference* "Advanced Inorganic Fibre Composites for Structural & Thermal Management Applications"

Co-Chairs: Mrityunjay Singh, *USA* *(Programme Chair)* Walter Krenkel, *Germany* Tatsuki Ohji, *Japan* *Members:* Rajiv Asthana, *USA* Alan Baker, *Australia* Wolfgang Brocks, *Germany* Tsu-Wei Chou, *USA* R.J. Diefendorf, *USA* Andrew L. Gyekenyesi, *USA* Jow-Lay Huang, *Taiwan* Toshihiro Ishikawa, *Japan* Chun-Gon Kim, *South Korea* Hai-Doo Kim, *South Korea* Pierre Ladeveze, *France* Jacques Lamon, *France* Javier Llorca, *Spain* Lalit Mohan Manocha, *India* Sanjay Mathur, *Germany* Sergei T. Mileiko, *Russia* Andreas Mortensen, *Switzerland* Roger Naslain, *France* Kiyohito Okamura, *Japan* Dieter Sporn, *Germany* Vijay K. Srivastava, *India*

ABSTRACTS

ABSTRACTS

CIMTEC 2010

12th International Ceramics Congress

June 6-11, 2010

OPENING SESSION

Plenary Lectures

C:PL1 **Nanoscience and Nanotechnology**
S. Iijima, Faculty of Science and Technology, Meijo University, National Institute of Advanced Industrial Science and Technology /Nanotube Research Center, SAINT and NEC

Nanoscience deals with nano-scale structures of materials and therefore controlling the structures is crucial. A typical example of nanostructures is carbon nanotubes whose many unique properties have been investigated theoretically and experimentally, and brought a new concept of materials into condensed matter physics. More importantly, nanoscience is closely related to nanotechnology and thus to industrial applications as we see in many fields of carbon nanotube research. An important issue for nanoscience research is characterization of the materials and many methods have been developed. In the case of carbon nanotubes their exact atomic structures are determined by means of electron microscopy, Raman and photoluminescence spectroscopy, etc., where sometimes commercially available instruments are not sufficient enough and need substantial modification for each particular purpose, where "do it yourself" becomes important. As examples mentioned above we demonstrate some latest results on structural characterization of carbon nanotubes(1-5), graphene(6), and boron nitride thin films(7), including "monatomic carbon strings that have been successfully made and observed in our laboratory(8).

1) K. Suenaga et al, Nature Nanotech. 2, 358 (2007); 2) Z. Liu et al, Nature Nanotech., 2, 422 (2007); 3) Y. Sato et al, Nano Lett, 7, 3704 (2007); 4) C.H. Jin et al, Nature Nanotech. 3, 17 (2008); 5) C.H. Jin et al, PRL, 101, 176102(1)-(4) (2008); 6) Z. Liu et al, PRL, 102, 015501 (1)-(4) (2009); 7) C.H. Jin et al, PRL, 102, 195505 (1)-(4) (2009); 8) C.H. Jin et al, PRL, 102, 205501 (1)-(4) (2009).

C:PL2 **Ceramics in New Energy Technologies**
Yet-Ming Chiang, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

Worldwide concerns over energy supply and climate change have created a need and opportunity for the development of new energy technologies in the area of storage and generation, many of which fundamentally depend on materials innovations. There is furthermore a need to accelerate these innovations to societal impact much more quickly than has been the historical norm. This talk will give several case studies on the use of electrochemically active ceramics in electrical energy storage, emphasizing the connection between basic phenomena, such as phase transformations, sintering processes, fracture and fatigue, and colloid chemistry, and the practical performance of devices. Opportunities for future advances will be highlighted.

C:PL3 **Computer Modelling as a Tool in Materials Science**
Richard Catlow, Department of Chemistry, University College London, London, UK

Computer modelling techniques are now used very widely in chemical, physical and biological sciences, especially in understanding the behaviour of complex systems at the molecular level. This lecture will highlight their application to materials science where the impact has been substantial in recent years. Special emphasis will be given to six important and topical areas: - Crystal structure prediction; - Guiding and understanding synthesis
- Modelling defects and Ion transport; - Modelling nucleation and growth; - Understanding reactivity at the molecular level; - Modelling structures and properties of nano-particles; Applications to oxides, microporous silicates sulphides and molecular crystal will be discussed. Future prospects and developments in the field will be considered.

Symposium CA

CERAMIC POWDERS: SYNTHESIS, PROCESSING AND SINTERING

Oral Presentations

Session CA-1
Powder Synthesis and Characterisation

CA-1:IL01 **Hydrothermal Synthesis of Functional Ceramic Particles**

Junichi Hojo*, Miki Inada, Naoya Enomoto, Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan

Hydrothermal process has been applied for synthesis of various oxide particles. One of strong tools is a microwave irradiation. Microwave can heat up water rapidly due to acceleration of molecular movement, leading to short reaction time compared to a conventional hydrothermal process and outstanding morphological and phase changes in product. Furthermore, microwave is absorbed in dielectric solvent, leading to selective heating of solvent. This behavior has been applied to synthesis of various oxide particles. TiO2 particles were prepared in anatase-like and rutile forms by self-hydrolysis of TiOCl2. The microwave irradiation enhanced the formation of anatase-like TiO2 nanoparticles. BaTiO3 nanoparticles were also obtained under microwave irradiation by aging of precursor prepared from BaCl2 and TiOCl2. These results mean that the microwave irradiation accelerates the dissolution of precipitated precursor and the nanoparticles formed under supersaturated solution. SiO2 mesoporous particles were prepared by microwave-emulsion process. Water solution of partially-hydrolyzed Si(OC2H5)4 with an organic template was dispersed in hexane and then heated by microwave irradiation. Because of the selective heating of water droplets, spherical SiO2 particles formed with mesopores.

CA-1:IL02 **Microemulsions as Reaction-Templates for the Synthesis of Novel Oxide-based Polar Electroceramics**

C. Pithan, Institute for Solid State Research, Forschungszentrum Jülich GmbH, Jülich, Germany

In the field of oxide-based polar electroceramics, such as di-, ferro- or piezoelectrics, the use of micellar systems (microemulsions) as reaction-templates for material synthesis offers a number of important advantages and unique opportunities regarding the design of novel nanostructured functional materials. During particle formation nucleation and growth are - in the ideal case - completely confined to the ultrasmall space of individual micelles and consequently well defined powders regarding size and agglomeration degree down to the primary structure level may be obtained for further ceramic processing. In many technologically relevant cases a liquid phase usually serves as a precursor. If correctly adjusted, the chemistry of the microemulsion allows the preparation of colloidal solutions that may be used for the deposition of thin films via spin-coating or ink-jet printing. A new material concept consists in the preparation of nanocomposites through hybrid solutions based on molecular precursors that are combined with nanoparticles of a microemulsion derived organosol. The present contribution addresses some general principles of synthesis and processing as well as some exemplarily chosen material systems illustrating some possible electroceramic applications.

CA-1:IL04 **Synthesis of Nitride (nano-)powders from Single-Source Preceramic Precursors: Potentialities as Building Blocks of Nitride Workpieces by Additive-free Sintering**

Samuel Bernard[1]*, Vincent Salles[1], Sylvie Foucaud[2], Alexandre Maître[2], Philippe Miele[1], [1]Laboratoire des Multimateriaux et Interfaces (UMR CNRS 5615), Université Lyon1, Université de Lyon, Villeurbanne Cedex, France; [2]SPCTS (UMR CNRS 6638), Faculté des Sciences et Techniques, Limoges, France

The pyrolysis of preceramic precursors represents an useful pathway for preparing various non-oxide ceramics with a controlled chemical composition and in complex shapes when coupled with convenient shaping processes. There are two strategies to generate such materials starting from single-source molecules. In a first strategy, the molecule-to-ceramic transformation process usually involves a complex sequence of chemical and physical changes through polymeric intermediates. This strategy offers a multi-step access to powders in micrometric size. In a second strategy, the transformation process is an one-step access to nanopowders. As examples of designing nitride (nano)-powders from single-source preceramic precursors, the presentation will be devoted to the one-step access of zero dimensional (0D) boron nitride nanopowders using the spray-pyrolysis of the single-source borazine molecule. The synthesis of the nanoparticles is described and discussed. Complete characterization has been performed. We have explored the potentialities of (nano)powders as building blocks to design 3D BN workpieces by additive-free sintering.

CA-1:IL05 **Convenient Hydrothermal Pathways to Functional Nanostructured Oxides: Methods, Mechanisms and Materials**

G.R. Patzke, Institute of Inorganic Chemistry, University of Zurich, Switzerland

The manifold properties and applications of oxide materials are indispensable for a future nanotechnology and the flexible structural chemistry of oxides provides an inexhaustible pool of compounds. However, the technically convenient transfer of complex oxides onto the nanoscale still remains a challenge. We focus on the development of robust and one-step hydrothermal approaches to functional oxides and on the elucidation of their mechanistic pathways with in situ methods. Methods: Microwave-hydrothermal methods are often superior to the conventional strategy. We have applied them upon the synthesis of nanoscale Zn/Cu-gallium spinels that are promising catalytic materials, e.g. for methanol synthesis. From mechanisms to materials: We have investigated the hydrothermal formation mechanisms of W/Mo-oxide nanomaterials that follow different pathways as a function of shape-controlling alkali cations. The emerging nanostructured W/Mo-oxides with a channel structure motif are now implemented as sensor materials.[1, 2]

[1] Y. Zhou, N. Pienack, W. Bensch, G.R. Patzke, Small 2009, 5, 1978.
[2] R. Kiebach, N. Pienack, W. Bensch, J.-D. Grunwaldt, A. Michailovski, A. Baiker, T. Fox, Y. Zhou, G.R. Patzke, Chem. Mater. 2008, 20, 3022.

CA-1:IL06 **Microstructural Tailoring of YAG and YAG-containing Nanoceramics Through Advanced Synthesis Routes**

Paola Palmero*, Laura Montanaro, Dept. of Materials Science and Chemical Engineering, Politecnico di Torino, LINCE lab., INSTM PoliTO R.U., Torino, Italy

Y3Al5O12 (YAG) shows interesting properties for mechanical and functional applications. Its cubic structure makes reliable the production of polycrystalline transparent materials for solid-state lasers and optical windows, for which highly pure powders, able to sinter up to full density are required. Recently, the strengthening effect of YAG fine grains into various ceramic matrices was also highlighted, thus promoting the development of composite materials for thermo-mechanical applications. This papers deals with different synthesis processes to produce pure, nano-crystalline YAG powders. Firstly, the co-precipitation route starting from yttrium and aluminum inorganic salts was investigated, underlying the role of the precipitation temperature as well as of the inorganic precursor (chlorides or nitrates) on the phase development. Secondly, YAG powders were produced by thermal decomposition of yttrium and aluminum nitrates in presence of a reducing agent. Finally, commercial alumina powders were doped with an yttrium salt, for producing both YAG as well as alumina-YAG composite materials. After free-sintering, beside high purity, a very homogeneous microstructure was yielded, in which 300 nm-sized YAG particles were well distributed into a micronic alumina matrix.

CA-1:L08 Ceramic Matrix Composites in the Alumina/YAG System

Radoslaw Lach, Krzysztof Haberko*, AGH University of Science and Techniology, Faculty of Materials Science and Ceramics, Krakow, Poland

Preparation technique of the particulate composite materials in the alumina/YAG system were studied. Within alumina particle suspension yttria precursor was precipitated with ammonium carbonate. Drying and calcinationa at 600 °C resulted in the mixture of alumina and yttria particles. The latter being much finer than alumina particles. This mixture was additionally homogenized by short attrition milling in an aqueous suspension of pH which level was selected on the basis of zeta potential measurements. It was found that acidic conditions (realized with HNO3) result in hard agglomerates. Such powders showed poor sintering ability and not homogenous second particles distribution. Much better properties were observed in case of powders homogenized under basic condition. They give dense materials composed of YAG inclusions of sizes several times smaller than shown by alumina grains and evenly distributed within the matrix. YAG particles result from the reaction of Y2O3 with Al2O3 during heat treatment. Some compositions show fracture toughness essentially higher than observed in pure alumina polycrystals.

CA-1:L09 New Route to Synthesize Silicon-substituted Hydroxyapatites

M. Zymelka*, D. Marchat, D. Bernache-Assolant, LPMG Laboratory UMR 5148 (CIS Center), Ecole Nationale Supérieure des Mines, Saint-Etienne, France; J. Chevalier, MATEIS Laboratory UMR 5510, Institut National des Sciences Appliquées, Lyon, France

Silicon-substituted hydroxyapatite (SiHA) is a highly promising material in the field of bioactive bone substitutes. First, incorporation of Si into the apatitic lattice seems improving the osteoconductive ability of hydroxyapatite. Second, silicate groups allow to envisage grafting of SiHA surface by cell-adhesive peptides in order to enhance implant osseointegration. The main goal of this study is to develop a new generation of bone substitutes which could cause and control the new bone growth. SiHAs were prepared by an aqueous precipitation method. An innovative protocol was set up to generate soluble silicate ions SiO44- from TEOS via a sol/gel route. The precipitation kinetic of SiHA was studied for the stoichiometric coefficients x=0.25 and x=0.50 in the theoretical formulation Ca10(PO4)6-x(Si04)x(OH)2-x. Both SiHA compositions were prepared at 50 °C, pH value of 9.5 and 11.0, and a maturation time ranged from 0 to 24h. Results show that a pure SiHA phase is formed at pH 11.0 and a maturation time higher than 2 hours. An exchange reaction between the precipitate and the bulk solution occurs throughout the maturation time. More, the silicate ions speciation (SiO44-, HSiO43-, etc) looks to be a key issue for precipitation of a pure SiHA phase thermally stable.

CA-1:IL10 Different Approaches for the Synthesis of Nanometric and Nanorods of Sr-doped LaPO4

M.T. Colomer, Instituto de Cerámica y Vidrio, CSIC, Cantoblanco, Madrid, Spain

Amongst all rare-earth orthophosphates, lanthanum orthophosphate, LaPO4, is perhaps the one presenting a broader range of applications in different areas of technological interest. Thus, monoclinic monazite-type LaPO4 presents very high melting point (>2000ºC), extremely low water solubility and chemical and thermal stability and, therefore, is currently under consideration as ceramic matrix for immobilizing high-level radioactive waste. Doped with cerium and terbium, LaPO4 is a commercially applied lamp phosphor while if doped with strontium, becomes a high-temperature proton conductor. As is well-known, not only the size but also the morphology of the particles can improve the properties of these materials. For that reason, numerous methods for the synthesis of oxides as nanoparticles and nanorods with desired particle size and controlled morphology have been developed. The resulting nanomaterials have recently gained interest and importance based on their novel properties associated with their reduced dimensionality and their potential application in nanotechnologies. Due to all these applications and possibilities, finding new methods to prepare LaPO4 and doped-LaPO4 is an area of interest in materials science. The present work describes different routes, such as combustion synthesis, mechanochemical milling, and microwave-assisted synthesis in order to obtain nanoparticulate powders and nanorods of rhabdophane and monazite Sr-doped LaPO4.

CA-1:IL11 Flame Synthesis of Ceramic Particles

Y. Takao, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan

We present a ceramic-powder preparation via flame synthesis assisted by DC arc. Gamma-aluminum oxynitride(AlON) spinel is a heat-resistance material with high thermal conductivity; but its raw powder is in nonspherical and aggregated state. Cosmetic requires high protection of UV rays, high transparent-looking and smooth-textured touch; but the simultaneous attainment is difficult. Flame synthesis assisted by DC arc plasma realizes a high reaction-speed of nonoxide(AlON) and composite(cosmetics) powders preparation (that combines economic efficiency in parallel). We discuss the influence of the free energy, reaction temperature and speed. And the resultant achievement of material properties also discussed.

CA-1:L12 Detection Limit of XRD Phase Quantification

N. Doebelin*, M. Bohner, RMS Foundation, Bettlach, Switzerland

Powder XRD in combination with Rietveld refinement is a powerful tool to analyze the crystalline phase composition of ceramic materials. As opposed to chemical analyses, it is sensitive to the crystal structure, which allows to identify chemically similar but structurally different phases. However, this technique is not very sensitive, and detection limits between 0.2 and 1.0 wt-% are not unusual. Random noise caused by the detector, as well as peaks overlapped by strong phases, increase the detection limit and cause systematic errors. In order to analyze the effect of these systematic errors, synthetic diffraction patterns simulating a biphasic calcium phosphate mixture with a given device setup were created. The patterns were refined using the same structural models as used for the simulation, with the only refined parameter being the scale factor of both phases. The results were compared with the known synthetic phase composition. Small amounts of HA (0.1-10.0 wt-%) in an a- or ß-TCP matrix were systematically underestimated by 0.3 wt-%. ß-Ca-pyrophosphate in ß-TCP was underestimated by 1.0 wt-%, and ß-TCP in a-TCP was underestimated by 0.5 wt-% in the same range. In all cases, refinements of 20, 30, and 50 wt-% of the secondary phase were accurate within 1 standard deviation.

CA-1:L13 One-step, Low-temperature, Microwave Assisted Synthesis of Barium Titanate Nanocrystalline Powders of Tunable Size

S.A. Veldhuis*, T.M. Stawski, J.E. ten Elshof, O.F. Göbel, D.H.A. Blank, University of Twente, Inorganic Materials Science Group, AE Enschede, The Netherlands

Barium titanate (BTO) is used as a high-k dielectric material in multi-layer ceramic capacitors. The minimum BTO thickness that can be achieved commercially with the state of the art tape casting methods is about 0.5 µm, which implies the use of starting powders with a particle size of ca. 100 nm. Further downscaling requires finer powders and new deposition techniques. Here the low-temperature synthesis of nano-sized crystalline BTO is presented. The process led directly to crystalline powder (5-50 nm), without any further calcination steps required. Barium titanate was synthesized from titanium isopropoxide and barium hydroxide in benzyl alcohol, at temperatures up to 175°C. As-synthesized powders exhibited a fully developed crystalline structure and a narrow size distribution. Electron microscopy and X-ray diffraction indicated that the size of crystallites depended mainly on the amount of water present in the system (contained as crystalline water or added externally). That observation enabled fine-tuning of the nanoparticle sizes. The organic impurity content in the product was investigated by thermal gravimetry/scanning calorimetry. By employing microwave heating the synthesis time was reduced from 2 hours to 15 minutes.

CA-1:L15 Synthesis, Up-conversion Luminescence and Sensing Properties of Trivalent Rare Earth Ion Doped CeO2 Powders

L. Baca*, H. Steiner, N. Stelzer, AIT Austrian Institute of Technology GmbH, Advanced Materials and Aerospace Technologies, Seibersdorf, Austria

The synthesis of Yb (III)- and Er(III)- co-doped cerium oxide powders by inverted co-precipitation from aqueous Yb, Er and Ce nitrate solutions followed by heat treatment at 1000 °C and 1500 °C, respectively, is presented. The influence of different precipitating agents on the phase evolution of trivalent rare earth ion doped CeO2 powders and their upconversion photoluminescence properties have been studied under 980 nm laser excitation. The results show that the upconversion luminescence intensity of the green and red upconversion is strongly dependent on the ratio of doping additives as well as the precipitating agent. Measurements of the photoluminescence intensity of sintered CeO2 samples revealed a strong dependence and sensitivity to temperature. The photoluminescence intensity increases with decreasing temperature and shows hysteresis behaviour during the thermal cycling of the sample.

CA-1:L16 Ultra-fine WC-Co Composites Prepared by Nitride Conversion Method and Their Properties

Yan-Mei Kan*, Shi-Kuan Sun, Guo-Jun Zhang, State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Shanghai, China

WC-Co cemented carbide has attracted considerable attention for use as a cutting tool, rock drill tips and other wear-resistant components because of its superior mechanical properties. It has been recently reported that ultra-fine grained WC-Co composite exhibit superior mechanical properties and abrasion-resistance in comparison with traditional WC-Co composite with grain size larger than 0.5 micro. However, limited by the quality of WC-Co nano-powder and the sintering technique, it is difficult to prepare ultra-fine WC-Co composite. This poses an obstacle for further improvement of the properties of the material. Thus in this study, WC-Co nano-powder was synthesized through an innovative nitride conversion method and the powder was compacted by spark plasma sintering. Three steps, preparation of high mixed WO3-CoO precursor, nitration of the oxides and carbonization of the nitrides, were included in the powder synthesizing process. The characteristics of synthesized powder, sintering behavior, mechanical properties and microstructure of the bulk cemented carbides were investigated. The relationship between microstructure and mechanical properties of the WC-Co composite was also discussed for a deep understanding of the grain size dependence of the material.

CA-1:L17 Synthesis of Ceramic Materials from Waste Residues

S. Portofino*, S. Galvagno, ENEA, C.R. Portici, Portici (NA), Italy

In the frame of a wide research programme devoted to the matter recovery from waste by means of thermal processes, particular efforts have been put into the study of biomasses and waste residue of peculiar composition, which could be used as precursors for ceramic materials. Rice shells are waste biomasses coming from the purification process of rice, which show a high carbon and silica content. The exploitation of these peculiarity promoted a series of experimental activities, aimed at the production of ceramic materials through high temperature carbothermal synthesis reactions. The synthesis products were characterised by X Ray Diffraction (XRD) and scanning electron microscopy (SEM) and the data confirmed the production of ceramic silicon nitride (Si3N4) at high yield and purity, under the adopted process parameters.

CA-1:L18 Solvothermal Synthesis of ITO Nanoparticles Precisely Controlled in Size and Shape

A. Muramatsu*, T. Sasaki, Y. Endo, Y. Doi, K. Kanie, Institute of Multidisciplinary Research for Advanced Materials,Tohoku University, Sendai, Japan

Tin-doped indium oxide (ITO) have been much investigated due to many TCO applications. The preparation methods of ITO have been reported, mainly based on the combination of the liquid-phase synthesis with succeeding thermal treatment for the crystallization. However, the precise control of ITO particles in size, shape, and structure simultaneously has never been succeeded, because of difficulty in strict separation of nucleation and growth, and crystallization in rather low temperature. In this paper, highly crystalline ITO nanoparticles with narrow size distribution were successfully prepared directly in one step from the mixed solution of indium and tin salts by the solvothermal method with ethylene glycol as a solvent. Also, their size was easily operated with changing conditions, such as aging period and NaOH concentration. This technique was based on the Gel-Sol method, including the strict separation of the nucleation and particle growth by controlling solution conditions, the perfect inhibition of tremendous coagulation between growing particles by fixing them in the gel network to avoid Brownian motion. In addition, we are use polyol as organic solvent in place of water, in order to regulate the water content as well as to maintain better atmosphere for ITO synthesis.

CA-1:L20 Challenges in the Synthesis of Metal Fluorides via Microemulsion Route

Ali Saberi*, Monika Willert-Porada, Faculty of Engineering Science, University of Bayreuth, Bayreuth, Germany

The low-phonon energy characteristic of fluorides particularly in the IR range has attracted the attentions as fascinating materials for up- and downconversion application. In this study zirconium fluoride, aluminium fluoride, and NaYF4 co-doped with Er3+/Yb3+ were synthesized by precipitation in reverse microemulsions of water in cyclohexane stabilized with polyoxyethylene octyl phenyl ether (Triton X-100). The results showed despite the fact that the particle size of synthesized powder decreases by increasing the mole ratio of emulsifier to water, the synthesized powders are suffering from the residue emulsifier which can affect the up- and downconversion properties. This article deals with the influence of residue emulsifier on the up- and downconversion efficiency of synthesized fluorides as well as the modification of procedure to get phase pure metal fluorides.

CA-1:L21 Sol-gel Synthesis Assisted by Supercritical CO2 - A Flexible Process for Ceramic Powder and Membrane Preparation

Audrey Hertz[1]*, Véronique Durand[1], Stéphane Sarrade[1], Christian Guizard[2], Anne Julbe[3], Jean-Christophe Ruiz[1], Frédéric Charton[1], [1]CEA, DEN/DTCD/SPDE/LFSM, Bagnols sur Ceze, France; [2]Lab. de Synthese et Fonctionnalisation des Céramiques, FRE 2770 CNRS-Saint-Gobain C.R.E.E., Cavaillon, France; [3]Institut Européen des Membranes, UMR 5635 CNRS-UMII-ENSCM, UM2-CC047, Montpellier, France

The increasing interest in supercritical fluids for synthesizing inorganic materials stimulated the development of new processes for production of nanophased powders/layers with controlled characteristics. Original processes based on sol-gel synthesis assisted by supercritical CO2 (SC-CO2) have been developed at the Supercritical Fluids and Membranes Laboratory (CEA). Unusual powder structures/morphologies have been evidenced and co-solvent characteristics have been proved to influence powder specific surface area and crystallite sizes. The development of a new semi-continuous process also enabled to tailor powder morphology by controlling hydrodynamic parameters (injection speed and stirring rate). Especially, yttria-stabilized zirconia prepared with this method are composed of 5-7 nm crystallites aggregated in spherical nanoparticles (<100nm) and yielding particularly high specific surface areas (up to 250 m2/g). These Y-ZrO2 powders can be compacted/deposited and sintered to prepare nanosized dense membranes for ionic conduction. Finally, SC-CO2 sol-gel processes can also be adapted to directly prepare gas separation membranes. In particular, an innovative process has been developed in our team to coat tubular porous ceramic substrates with microporous silica-based layer.

CA-1:L23 Nano-sized BT Powder with High Tetragonality Synthesized by Hydrothermal Method

Changhak Choi*, Kumjin Park, Hyungjoon Jeon, Hyeyoung Baeg, Sanghyuk Kim, Sanghoon Kwon, Kangheon Hur, LCR Division, Samsung Electro-Mechanics Co. Ltd, Suwon, Korea

Nano-sized BaTiO3 (BT) powders with uniform size distribution and high tetragonality (c/a) were prepared by modified hydrothermal method. The relation between reaction condition and tetragonality of BT powder were investigated with kinetic and thermodynamic consideration. The distribution of phases in a BT powder was analyzed with synchrotron XRD and Rietveld simulation. Tetragonal, cubic and gradient phase were existed in a BT powder with volume ratio of 0.77:0.03:0.20 and tetragonality of 1.0099, 1.0000, 1.0050, respectively. Moreover, the pore volume in BT powder was measured by STEM (scanning transmission electron microscope). The apparent tetragonality was calculated with a BT particle model which have different pore volume and phase’s distribution. In order to obtain the high tetragonality of nano-sized BT powder, the cubic and gradient layer should be thin and the tetragonality of tetragonal region should be high. In this work, 70nm-sized (in diameter) BT powders with high c/a of 1.008 and uniform size distribution could be obtained by hydrothermal method.

CA-1:L26 Production of Nanopowders with the Help of Fiber Laser

M. Ivanov*, Yu. Kotov, O. Samatov, Institute of Electrophysics, Ural Division of Russian Academy of Sciences, Ekaterinburg, Russia

Development of an efficient technology to produce nanopowders for nanostructured materials with improved mechanical, novel electromagnetic and optical properties is still of current importance. Nanoparticles can be made by means of laser-assisted material evaporation and subsequent vapor condensation. The method provides high-purity weakly agglomerated nanopowders with narrow grain size distribution, and can be applied to various materials. However, up to these days this technique has not found wide recognition because of a low output rate and high energy consumption. This report deals with the production technology and characteristics of nanopowders produced with the help of Yb-doped fiber laser. We produced weakly agglomerated nanopowders of complex compounds with particles size ~10 nm, narrow size distribution, high productivity and quite low energy consumption. Y2O3 - stabilized ZrO2 (YSZ), Al2O3+YSZ, CeGdO, Nd:Y2O3, Nd:YAG, ZnS nanopowders for fuel cells, optical ceramic and phosphor were prepared. Data for the nanopowders characteristics, as well as output rate and energy consumption are discussed in the presentation. The evaporation of materials with the help of the fiber laser was proved to be an efficient method for commercial production of the fine nanopowders.

Session CA-2
Colloidal Processing

CA-2:IL02 Development of Environmentally-friendly Process Using Ceramic Colloidal Processing on Ceramic-polymer Composite Materials

Yuji Hotta*, Katsuya Sato, Koji Watari, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan

In recent years,ceramics-polymer materials with superior ceramic properties, e.g. heat-conductivity, insulation, mechanical strength, weatherability and so on, have been attracted attention from viewpoint of materials specifications and manufacturing cost. In order to produce ceramic-polymer composite materials, it is important to disperse particles and to increase amount of particles in polymer. However, generally, ceramic particle surface is modified chemically to disperse particles well in polymer. Therefore, the environmental load on manufacturing is worried about. From this issue, we studied the environmentally-friendly process for preparation of high-solid loaded ceramic-polymer composite materials without chemical modification by using ceramic colloidal processing. As a result, by the selection milling method, the high solid loaded ceramic particles could be dispersed uniformly in polymer at primary particle level without chemical modification. The ceramic colloidal processing method used in this study that involves neither any chemical modification to disperse ceramic particles nor any complicated chemical reaction is expected as manufacturing process for ceramic-polymer composites with low environmental impact.

CA-2:L04 Experimental and Simulation Study of Self-arrangement by Heteroagglomeration in Dilute, Model Ceramic Suspensions

M.A. Piechowiak*, A. Videcoq, C. Pagnoux, F. Rossignol, SPCTS, ENSCI, Limoges, France; R. Ferrando, M. Cerbelaud, Dipartimento di Fisica dell'Università di Genova, Genova, Italy

In colloidal processing, the preparation of ceramic suspensions is a crucial step for the final properties of the product. To understand, predict and control the behaviour of suspensions is therefore of a particular interest. Our aim is to highlight the key parameters responsible for the particles arrangement in model suspensions by comparing experiments and Brownian dynamics simulations. Heteroagglomeration has been recently studied in our Laboratory, especially with commercial powders[1], while the present system consists of model, spherical, oppositely charged and equally sized particles based on silica. The experimental study includes (i) the synthesis of core-fluorescent particles, surrounded by a silica or an aluminium monohydroxide shell in order to obtain either negatively or positively charged particles, (ii) the suspension characterization (pH, conductivity, zeta potential measurements, sedimentation test,.) and (iii) the imaging of the particles arrangement (by confocal and cryo- scanning electron microscopes). The suspension behaviour is studied as a function of dilution and composition. Finally the experimental results of such suspensions are qualitatively and quantitatively compared to the simulation results.

[1] M. Cerbelaud, et al, Langmuir, 24 (2008) 3001-30

CA-2:L05 A Study of the Dispersion of Boron Carbide in an Aqueous Suspension

A.C.J. Heaton*, DSTL, Porton Down, Wiltshire, UK; J.G.P. Binner, Loughborough University, Leicestershire, UK; R.N.J. Taylor, AWE, Aldermaston, Berkshire, UK

Boron carbide is one of the hardest materials known, however to achieve this components must be sintered to high densities. To aid in the achievement of this the dispersion of boron carbide powder within an aqueous suspension was studied. Work carried out on the production of suspensions containing Tetramethylammonium Hydroxide (TMAOH) and Dispex A40 will be discussed in particular the creation of suspensions with low viscosities and up to 70 wt% boron carbide content. When slip cast these suspensions produced green components of greater than 65% of theoretical density allowing the achievement of high sintered densities.

CA-2:IL06 When Specific Interparticle Forces Lead Colloidal Particles to Self-assemble in Dilute Suspensions: Simulation and Experiment

A. Videcoq*, M. Piechowiak, C. Pagnoux, F. Rossignol, SPCTS, UMR 6638, ENSCI, CNRS, Limoges cedex, France; M. Cerbelaud, R. Ferrando, Dip. di Fisica dell'Università di Genova, Genova, Italy

Colloidal processing of ceramics requires the preparation of suspensions whose characteristics strongly influence the final properties of the component. The control of the particles arrangement in suspension is of a particular interest to get reliable shaping processes. By a close comparison between experiment and modelling, the aim of the present work is to highlight the key parameters responsible for the structuring in suspensions. Dilute aqueous suspensions containing two kinds of particles, that are prone to heteroagglomeration, have been recently considered in our laboratory (SPCTS, UMR 6638). They have been studied, both numerically and experimentally, as a function of the number and size ratios between the two kinds of particles. The simulation methods used are Brownian Dynamics and Monte Carlo minimization. A good qualitative agreement has been obtained between experiment and simulation results. It concerns both the tendency towards agglomeration or dispersion and the intimate organization of the particles in suspension. The results emphasize the prediction capacity of the simulations, what can be interesting for controlling the particles assembling in such binary mixtures and especially the multi-scale porosity in the structure.

CA-2:IL07 Modified Surfaces of Ceramic Particles Finely Tuned for Ceramic Forming Processes

K. Sato, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan

Most ceramics are produced as particle assemblages made dense by firing. Forming is an important step prior to densification and determines the properties of the final products. One important goal to be achieved in forming processes is to fully disperse solid particles in a liquid medium to avoid the generation of agglomerates. A novel preparation method of aqueous ceramic slurries will be described in the presentation. The method can be characterized by creating a chemically grafted dispersant molecule layer on particles' surfaces which is very soluble in water. The tuned configuration of dispersant molecules causes neither bridging nor depletion flocculation but induces steric repulsion effectively. The obtained aqueous slurry is quite stable and yields green bodies with high relative density.

CA-2:L08 Influence of Energy Input on Suspension Properties

A. Meyer*, A. Potthoff, K. Lenzner, Fraunhofer IKTS, Dresden, Germany

Nano particles are increasingly used in ceramic industry. Because of the minor expenses related with it, for its production the top down process can often be used instead of the bottom-up synthesis process. The possible reduction ratio of the particle size during grinding strongly depends on the stability of the particles in the slip to prevent agglomeration. In-depth knowledge of the interactions between the powder and the additives is needed to adjust the characteristics of the slip in a defined manner and to control the production of nanosized powders through milling, because interactions between powder and additives and the stabilizing effect of dispersing agents can significantly change during the grinding process. Results of changing interactions of a boehmite powder in water with commercially available dispersants based on polyacrylic acid as a function of the applied energy are presented. Measurements of the surface charge of the particles and simultaneous analyses of the viscosity of the slip and the adsorption behavior of the additives enable a direct detection of the changing interactions. The reasons for the varying interactions and the therewith connected loss of stabilization are discussed and the feasibility of milling of boehmite in a ball mill is presented.

CA-2:L09 Effects of Dispersion Surfactants on the Properties of Alumina - Carbon Nanotube (CNT) Nanocomposites

F. Inam[1]*, A. Heaton[2], P. Brown[2], T. Peijs[1,3], M.J. Reece[1,3], [1]Queen Mary University of London, Nanoforce Technology Ltd, London, UK; [2]Dstl, Porton Down, Salisbury, Wiltshire, UK; [3]Queen Mary University of London, School of Engineering and Materials Science, London, UK

Dispersion of multi-wall carbon nanotubes (CNTs) within an alumina matrix was performed using Gum Arabic (GA), Sodium Dodecyl Sulfate (SDS) and a combination of the two. Low loadings (0.5-1 wt%) of CNTs were dispersed using a bath ultrasonication method and analysed via UV-vis spectroscopy and agglomerate size analyser. The combination of GA and SDS produced the best dispersion compared to GA and SDS alone. Sintering of the alumina - CNT nanocomposites were carried out using Spark Plasma Sintering (SPS). Electron microscopy, electrical and mechanical characterisations of the sintered nanocomposites allowed evaluation of the effectiveness of the different surfactants. The combination of GA and SDS produced agglomerate free, homogeneous CNT alumina nanocomposites with higher electrical conductivity and fracture toughness as compared to those prepared using only GA or SDS.

CA-2:IL10 Interparticle Forces the Key to Colloidal Processing: from Porous Nanostructured Films to Transparent Polycrystalline Alumina

P. Bowen[1]*, M. Stuer[1], Z. Zhe[2], U. Aschauer[3], [1]Laboratoire de Technologie des Poudres, EPFL, Lausanne, Switzerland; [2]Dept. of Physical, Inorganic and Structural Chemistry, Arrhenius Lab., Stockholm University, Stockholm, Sweden; [3]Dept. of Chemistry, Princeton University, Princeton, USA

The success of the final application of the ceramic depends on its microstructure which is governed by the quality of the starting powder and our capacity to form a green body, green tape or powder compact before the sintering or consolidation step. Almost all the methods in their conditioning and compounding pass via a ceramic suspension. Therefore powder dispersion and the prevention of agglomeration while preparing a ceramic suspension is of key importance. A simple to use software for the key interparticle forces, attractive (van der Waals) and repulsive (electrostatic, steric), has been developed. This program (Hamaker) is available on the LTP website (http://ltp.epfl.ch/page65254.html with complete documentation including the scientific background of each model. First a brief introduction to the various interparticle forces will be give and then several examples of its use to assess the conditions and dispersion stability of silicas and aluminas will be given. Examples for film casting of porous supports for ink-jet paper coating, filter pressing and the influence of agglomerates on microstructures and optical properties of SPS sintered transparent alumina will be used to illustrate the importance of the powder characteristics and degree of dispersion.

CA-2:IL11 Theoretical and Experimental Analyses of Colloidal Processing of Nanoparticles

Y. Hirata*, K. Matsushima, S. Baba, N. Matsunaga, S. Sameshima; Kagoshima University, Kagoshima, Japan

The stability of dispersed and flocculated colloidal particles under 1 atm and applied pressure was calculated thermodynamically with the activity and chemical potential defined by Henry's law and Raoult's law. The calculated result at 1 atm is represented by a colloidal phase diagram as functions of surface potential and solid content of suspension. Application of pressure accelerates the phase transition from dispersed to flocculated suspension. The phase transition pressure, which is observed in the applied pressure-suspension height relation during pressure filtration at a constant crosshead speed of piston, is affected by (1) particle concentration, (2) particle size, (3) surface potential (rate constant of flocculation), (4) degree of dissociation of polyelectrolyte dispersant and (5) applied electric field (DC and AC). The influence of above factors is discussed theoretically and experimentally.

CA-2:IL12 Colloidal Processing of Nanosized Titania Suspensions

Rodrigo Moreno, Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain

Nanostructured titania materials are receiving increased attention due to the wide number of applications in different technologies, such as catalysis, photovoltaics, etc. However, the preparation of concentrated suspensions of nanostructured powders requires a suitable control of the colloidal behaviour and the optimization of the rheological properties when particle concentration increases. The preparation of suspensions of submicrometric sized titania has been reported elsewhere, but information concerning nanosized titania powders is still scarce. On the basis of the existing literature the colloidal stability of nanosized titania suspensions is reviewed in this work. Different commercial nanosized titania materials are studied and compared, including powders and colloidal suspensions, and their mixtures. The preparation of stable suspensions of titania nanopowders is studied in terms of zeta potential measurements as a function of pH, type and concentration of polyelectrolytes, mixing time using an ultrasounds probe, etc. The preparation and rheological properties of concentrated suspensions with up to 30 vol.% solids is also reported. The performance of these suspensions for preparing bulk pieces by slip casting or reconstitution by spray or freeze drying is also reported.

CA-2:IL13 An Impact of Filter Pressing of Multicomponent Nanopowders on the Composite Microstructure

W. Pyda*, N. Moskala, L. Mirowska, AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Cracow, Poland

Elongated nanoparticles inserted into a ceramic matrix lose the shape during high temperature consolidation. Colloidal processing followed by filter pressing can solve this problem due to the strong impact on a decrease of sintering temperatures, giving fully dense materials. Detailed study is presented concerning behaviour of different in shape zirconia nanoparticles mixed with alumina during filter pressing and natural sintering. Three zirconia nanopowders composed of isometric, plate-shaped or needle-shaped nanocrystallites were prepared by using a precipitated zirconia hydrogel hydrothermally treated in the environment of a suitable mineralizer. Colloidal processing was used to prepare homogeneous mixtures of 10 vol. % of each zirconia nanopowder with a commercial alumina nanopowder. Peptized/hetero-flocked slurries were processed. The mixtures were dried to prepare a powder for cold pressing or leaved in the undried state for filter pressing. Green compacts were naturally sintered in air. The nanopowders were characterized with HREM, BET, XRD and DLS, and the green compacts by mercury porosimetry. The sintered materials were observed by using electron microscopy. Evolution of the shape of zirconia nanoinclusions was studied and the mechanism discussed.

CA-2:IL14 Hierarchical Porous Materials through Microfluidics

A.R. Studart, R.M. Erb*, Complex Materials, Department of Materials, Zurich, Switzerland

Porous materials can be produced using a number of different colloidal processing routes, including for example the selective removal of sacrificial templating building blocks from consolidated suspensions and emulsions. This approach is particularly suitable to obtain tailored porous materials, since the pore size and porosity can be independently tuned by changing the size and concentration of the sacrificial building blocks. While templating particles and surfactants with narrow size distribution are readily available for the formation of monodisperse pores ranging from 1nm to 10µm, bubbles and droplets often used as templating units at larger length scales usually display broad and poorly controlled size distributions. Microfluidic devices can help to overcome this limitation, since it enables the creation of monodisperse droplets within the size range 10-600 µm. In this talk, I will illustrate how microfluidics can be used to produce materials exhibiting precisely controlled porous structures with pores ranging from a few tens of nanometers up to millimeters in size. Hierarchical porous materials exhibiting this well-defined structure can potentially be used as scaffolds for tissue engineering, electrodes for fuel cells or catalytic supports in bio- and chemical reactors.

CA-2:IL15 Surface Characterization and Chemistry for Ceramic Powder Processing

Takashi Shirai, Nagoya Institute of Technology, Tajimi, Japan

The surfaces of ceramic powder have played a key role in their performances in many technological applications such as a high-temperature structural material, electronic packaging, and also in other fields where ceramic-metal bonding is used. In the case of alumina powders, the surface may contain an aluminum hydroxide phase, which can also generate surface condition differences in the alumina powders. The surface condition differences of the powders can influence their physical properties such as zeta potential, powder agglomeration and sintering behavior. Therefore, the investigation for hydration ability of powder surfaces is very important for ceramic manufacture. The objective of the present work is to understand the hydration behavior and interaction between surface hydroxyl groups and adsorbed molecules are studied by combining temperature programmed desorption mass spectrometry (TPDMS) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy techniques.

Session CA-3
Shape Forming and Compaction Mechanisms

CA-3:IL01 Printing Techniques for the Manufacture of Structures in the Micrometer Range

Andreas Roosen, University of Erlangen-Nuremberg, Institute of Glass and Ceramics, Erlangen, Germany

Printed electronics is an emerging technology in which electrically functional devices are deposited by printing methods. In contrast to vacuum deposition techniques, printing of organic or inorganic components is a low cost process, which is target on products like RFIDs, OLEDs, sensors, displays, or solar cells on flexible polymer carriers. The well-known screen printing process is an example for a very successful printing technique, which is based on inorganic materials and used on a large scale, e.g., to print circuits for microelectronic applications. But its resolution of 80 to 100 µm in lines and spaces is not low enough to print economically, e.g., thin film transistors. The paper gives an overview about printing techniques and their degree of resolution. It will address in detail the preparation of layers and structures by screen printing, inkjet printing, µ-contact printing, and Micro-Moulding-in-Capillaries (MiMiC), in which the latter can be used to print structures in the µm-range. Processing issues like the dispersion and stabilization of nano-sized powders to achieve homogenous pastes and inks of suitable concentration and rheological behaviour will be discussed. The characteristics of the deposited structures and their physical performance will be described and compared using the example of printed field effect transistors (FET).

CA-3:IL02 **New Developments in the Electrophoretic Deposition (EPD) of Structured Compacts and Coatings**

R. Clasen, Saarland University, Campus C6 3, Saarbrucken, Germany

The EPD has been proven to be an interesting process for forming compacts and coatings. As the deposition rate is independent of particle size, EPD is very effective especially for nanopowders. For aqueous suspensions, which are desirable for environmental reasons, a technical challenge is to solve the problems of the bubble formation due to the decomposition of water at the electrodes. This bubble formation for anodic deposition of negatively charged particles can be suppressed by oxidation of the electrode, the electrolyte (or any other addition), incorporation of a separating membrane, or pulsed currents utilizing non-linear effects. After a brief review of the state of the art new developments are presented to the deposition of structured compacts. While most of the rapid prototyping techniques are based on a layer-wise deposition, the EPD with microelectrodes offers new possibilities to get a homogeneous compact. For structured coatings an approach similar to laser printing (electrophotography) seems to be very promising. In both cases the bubble formation was suppressed by a combination of a membrane and oxidation of the electrolyte. Additionally, the potential and problems of pulsed currents were investigated.

CA-3:L03 **Influence of Different Suspension Properties on Internal Structure and Deformation Behaviour of Spray Dried Ceramic Granules**

S. Eckhard*, M. Fries, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany

Spray drying of suspensions of nano- or colloidal-disperse ceramic material is one of the most common agglomeration processes to improve handling and processing properties according to further processing steps. From literature and own research work it is known, that besides the added amount and kind of organics also the internal granule structure of spray dried ceramic granules as intermediate products for die pressing applications has strong influence on deformation behaviour and granule strength. By varying the properties of the starting suspensions granules with different internal micro- and macrostructures can be achieved by spray drying. It is necessary to characterize internal granule structures in a quantitative, objective and reproducible way following a suggested method. After the mechanical properties were investigated with deformation tests on single granules, correlations between internal granule micro- and macrostructure and mechanical properties of the granules (fracture deformation, fracture force, fracture strength) can be found. Additional the influence of different raw materials on resulting internal granule structures and therewith on mechanical properties was investigated by choosing sub-µm alumina primary particles and nano-scaled particles for granulation.

CA-3:L04 **New Low-toxic Water-Soluble Monomers for Gelcasting of Ceramic Powders**

Mikolaj Szafran*, Paulina Bednarek, Agnieszka Szudarska, Tadeusz Mizerski, Warsaw University of Technology, Faculty of Chemistry, Warsaw, Poland

Colloidal processes are applied in the fabrication of high-quality ceramic elements of complicated shape among which we can distinguish gelcasting, a method which combines conventional moulding from slips with polymer chemistry. The research made by authors concentrates on the synthesis of new low-toxic monomers with an acrylic group, which is able to polymerize in situ. The comparison of newly synthesized monomers such as glycerol monoacrylate and acrylic derivatives of saccharides will be presented. These derivatives are based on mono- and di saccharides, eg. glucose, fructose and sucrose. The application of these compounds will be shown for three ceramic powders: alumina, zirconia and mullite. The application of these monomers in the gelcasting process allows to obtain rigid green ceramic specimens without adding an external cross-linking agent to a slurry, what results in reducing amount of gases released to the atmosphere during polymer burnout. The rheological properties of ceramic slurries, properties of received elements in green and sintered state will be compared with those obtained with application of commercially available monomer 2-hydroxyethyl acrylate.

CA-3:IL06 **New Developments in Electrophoretic Deposition Processing**

Tetsuo Uchikoshi*, Tohru S. Suzuki, Yoshio Sakka, Nano Ceramics Center, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan

Electrophoretic deposition (EPD) is a colloidal process wherein ceramic bodies are directly shaped from a stable colloid suspension by a dc electric field. Compared to other advanced shaping techniques, the EPD process is very versatile since it can be modified easily for a specific application. EPD is also gaining increasing interest as a processing technique for production of novel inorganic nanostructured and nanoscale materials. Application of pulsed-DC enables to obtain smooth, bubble-free deposit from aqueous suspension. Dense uniform deposits can be obtained on non-conductive ceramic materials covered with conductive materials, such as conductive polymer. EPD in a strong magnetic field is one of promising processing techniques to fabricate crystalline-textured ceramic composites. It was found that by changing the angle between the directions of magnetic and electric fields during EPD, the orientation of the crystals in the deposit could be controlled. In this presentation, we will introduce our recent studies on EPD for variety of applications in structural and functional ceramics, and discuss its versatility and potentiality.

CA-3:IL07 **Improving the Porosity Features Control of Ceramic Cellular Components through a Modified Gelcasting Process**

M. Lombardi*, L. Montanaro, Dept. DISMIC-Politecnico di Torino, INSTM - R.U. PoliTO - LINCE Lab., Torino, Italy; S. Meille, J. Chevalier, Université de Lyon, INSA-Lyon, MATEIS, CNRS UMR 5510, Villeurbanne, France

An innovative procedure was developed combining a conventional gelcasting based on in situ polymerization of a natural gelling agent to a fugitive phase method, in which polyethylene (PE) spheres are used as porogen. By a suitable selection of the PE spheres and volume percentage, it is possible to determine some important porosity features of the final component, such as the mean pore size, the total pore volume, the pore geometry as well as the pore interconnection number and size. PE spheres are dispersed into a stable ceramic suspension under magnetic stirring; natural gelling additives are then added at 60°C. The suspension is poured under vacuum and the gelation takes place during cooling down to room temperature. Drying is performed in controlled humidity and temperature conditions. Finally, the green bodies are submitted to a controlled thermal treatment. The microstructure of the fired components is characterised by spherical pores surrounded by highly dense ceramic walls and struts. The effectiveness of this method has been demonstrated by applying it to ceramic powders different in terms of composition and size; alumina and hydoxyapatite-based cellular components have been prepared and fully characterized to demonstrate the versatility of the process.

CA-3:L08 **Processing and Superplastic Deformation of Zirconia-based Ceramic Nanocomposites**

K. Vanmeensel*, H. Sheng, A. Laptev, A.K. Swarnakar, O. Van der Biest, J. Vleugels, Katholieke Universiteit Leuven, Department of Metallurgy and Materials Engineering, Heverlee (Leuven), Belgium

The processing and deformation behaviour of electrically conductive ceramic nanocomposites with an average grain size below 100 nm is described. The composites combine a tough and strong yttria stabilised zirconia matrix with a hard and electrically conductive secondary carbonitride phase and were densified using the pulsed electrical current sintering technique (PECS). After densification, the prepared composite materials were deformed in situ in the PECS machine and the capability of superplastic shaping was demonstrated. The combined influence of the refined microstructure, as compared to micrometer sized composites, and the electrical current on both the densification and deformation behaviour of this type of composites is discussed in detail.

CA-3:L09 Saccharides Derivatives in Shaping of Ceramic Powders - New Monomers and Dispersants

Paulina Bednarek*, Mikolaj Szafran, Tadeusz Mizerski Warsaw University of Technology, Faculty of Chemistry, 3 Noakowskiego St. 00-664 Warsaw, Poland

Colloidal processes are used to produce a high-quality ceramic elements of complicated shape among which we can distinguish gelcasting, a method which combines conventional moulding from slips with polymer chemistry. The research made by authors concentrates on the synthesis of new low-toxic monomers on the basis of saccharides, which could be applied in gelcasting instead of toxic and commonly used acrylic substances such as acrylamide or 2-hydroxyethyl acrylate. The synthesized monomers are 3 acrylic-D-glucopyranose, 1-acrylic-D-fructiopyranose and monoacrylic saccharose. The application of these monomers in the gelcasting process allowed to obtain rigid green ceramic specimens without adding an external cross-linking agent to a slurry, what results in reducing amount of gases released to the atmosphere during polymer burnout. What is more, some of these saccharide derivatrives exhibit activity as dispersing agents for nanometric alumina. The work reports the research on application of new additives in gelcasting of alumina powders of different grain size. The properties of received elements have been compared with those obtained with application of commercially available monomer 2-hydroxyethyl acrylate.

Session CA-4
Sintering and Related Phenomena

CA-4:IL02 Evidence of a Microwave Effect on the Sintering of Y-TZP Powder

S. Charmond, C.P. Carry, D. Bouvard*, Laboratoire SIMAP, Grenoble Institute of Technology / Université Joseph Fourier / CNRS, Saint Martin d'Heres, France

It has been claimed and shown that most ceramic powders can be sintered by microwave at lower temperatures and during shorter times than in conventional sintering, which potentially allows for the development of finer and more uniform microstructures. However, definitive evidence of a genuine microwave effect on diffusion mechanism has not been given so far, due to difficulty of comparing microwave and conventional sintering in perfectly identical thermal conditions. This paper investigates the specific effects of the electric field on the densification and microstructure changes of zirconia nanomaterials. For this purpose a resonant single-mode cavity at 2.45 GHz has been used. The final densities and the microstructures observed by SEM were compared to those of the materials conventionally sintered at the same heating rate. A significant enhancement of the densification process under microwaves has been observed in the intermediate sintering stage (1200-1350 °C range). Besides, grain growth has been found to be mainly influenced by the sintering temperature rather than the heating mode. These results are interpreted in terms of sintering mechanisms.

CA-4:IL03 Sintering Kinetics of Powder Compact Containing Large Pores

Jingzhe Pan*, Fan Li, Department of Engineering, University of Leicester, Leicester, UK

It is commonly believed that a large pore does not shrink during sintering. Here "large" is defined by the number of grains surrounding a pore, which is known as the co-ordination number. A classical textbook theory predicts that a pore would shrink only if its co-ordination number is less than a critical value. It follows that grain-growth can be used as a means to eliminate large pores. In this talk, we will argue that the critical coordination number theory is misleading. Firstly the critical coordination number theory will be reviewed and a brief derivation of the theory will be provided. Secondly experimental and computer simulation evidences against the critical coordination number theory will be collected from previous works (Flinn, Bordia, Zimmermann, and Rödel, 2000, J. Eur. Ceram. Soc., 20, 2561-2568; and Pan, Ch'ng and Cocks, 2005, Mechanics of Materials, 37, 705-721) and presented. Thirdly it will be shown that the densification rate of a powder compact containing both large and small pores can be predicted using a simple analytical model (Pan, Cocks, Rodel, Huang and Ch'ng, 2009, Journal of the American Ceramic Society, 92, 1414-1418). It is concluded that grain-growth is always harmful to the elimination of the pores.

CA-4:IL04 Microstructural Anisotropy during Constrained Sintering

O. Guillon, Technical University Darmstadt, Darmstadt, Germany

During the sintering of ceramic layers or the co-firing of multilayered ceramics, radial shrinkage is inhibited at a large degree while densification takes place in the thickness direction. This geometrical constraint induced by another elastic or viscous material affects the densification kinetics and the microstructure of the sintering layer. This microstructural anisotropy changes with density and depends on the sintering mechanism (solid state diffusion, liquid phase sintering or glass densifying by viscous flow). Novel methods and parameters have to be developed to catch this evolution, from the image analysis of 2D polished cross-sections to high resolution synchrotron computed tomography.

CA-4:L05 Effect of Anisotropic Local Structure on Sintering Stress Tensor and Viscosities for Macroscopic Shrinkage in Sintering

F. Wakai*, Y. Shinoda, T. Akatsu, Secure Materials Center, Materials and Structures Laboratory, Tokyo Institute of Technology, R3-23-4259 Nagatsuta, Midori, Yokohama, Japan

Many sintering bodies shrink in an anisotropic manner, when the particle packing is not isotropic. Macroscopic shrinkage in sintering is described as a linear function of sintering stress tensor [F Wakai, Y Shinoda. Acta Mater 2009;57:3955] and viscosity tensor, which is determined by taking into account the grain boundary diffusion mechanism and the anisotropy in microstructure. Both sintering stress tensor and viscosity tensor are determined numerically for open pore structure with orthotropic symmetry (simple, body-centered structure, and face-centered structure) in three dimensions. These anisotropic models of the intermediate stage of sintering are characterized by the equilibrium surface. The deviatoric components of both sintering stress tensor and viscosity tensor are approximately proportional to the logarithm of the aspect ratio. The deviatoric sintering stress acts so as to deform the elongated particles to be more isotropic in most cases. These results in three dimensions agree well with those obtained in two dimensions.

CA-4:L06 Particle-based Simulations of Thin Film Sintering

T. Rasp*, A. Wonisch, T. Kraft, and H. Riedel, Fraunhofer Institute for Mechanics of Materials, Freiburg i. Br., Germany

During sintering of thin films that are constrained by a rigid substrate, anisotropic pore growth and crack initiation can be observed. This is most evident in the interface area where the substrate inhibits the in-plane shrinkage of the layer. The cracks can grow in time, which strongly affects the durability of the film to the point of complete failure. In order to make predictions about microstructure evolution and crack propagation of thin films a particle-based simulation approach is employed. It is based on the Discrete Element Method (DEM), in which each grain of the ceramic powder is regarded as a distinct particle that interacts with neighbouring grains. Therefore, effects like particle rearrangement and anisotropic orientation of pores are included in the simulation by design. This allows for a better understanding of the fundamental mechanism occurring during constrained sintering and allows determining critical parameters for crack initiation. First results on this topic are presented and compared with experimental data on the basis of solid state and liquid phase sintering for a fine grained alumina powder (Sumitomo, AKP 30).

This work is supported by the Deutsche Forschungsgemeinschaft (DFG) under contracts No. KR 1729/10-1

CA-4:L07 Modelling Multi-cracking in Thin Films during Constrained Sintering

Fan Li*, Jingzhe Pan, Department of Engineering, University of Leicester, Leicester, UK

The sintering of thin films is one of the common technologies to produce surface coatings and multi-layered systems. During the sintering process, the thin film is constrained by the substrate, which generates considerable stress. Crackings are often observed and are considered as one of the major problems in many applications. This paper presents a new numerical method in order to tackle the traditional difficulties in simulating multi-crackings during constrained sintering. Main features of the present method include: (i) the material data is represented by an anisotropic constitutive law, (ii) a new numerical scheme is developed for the crack initialization and growth based on the material point method, (iii) the 3D viscous film shrinkage model is solved using a dynamic scheme, and (iv) the random nature of the initial density is represented by statistical variabilities. It is shown that the model is capable of simulating the nucleation and propagation of multi-cracks. The simulated cracking patterns are shown to be consistent with experimental observations. Parametric studied are performed aiming at optimizing of the film coating process. The focus of the paper is on the numerical issues and demonstrating the capacity of the model.

CA-4:L08 Contribution of Discrete Element Simulation to the Analysis of Ceramic Aggregated Powder Processing

P. Pizette[1]*, C.L. Martin[1], G. Delette[2], F. Sans[3], D. Bouvard[1], [1]Lab. SIMAP-GPM2, Grenoble Institute of Technology / Université Joseph Fourier / CNRS, Saint Martin d'Heres, France; [2]CEA-Grenoble, DRT/LITEN/DTH/LEV, Grenoble Cedex, France; [3]AREVA/MELOX DT/DIP, Bagnols sur Cèze, France

Die compaction is a crucial stage to obtain sintered products of optimal quality from ceramic powders. Adequate green strength is required to minimize initiation of microcracks that may appear during ejection. Such microcracks would result in unacceptable defects after sintering. Here, the compaction stage of ceramic aggregated powders and the resulting strength of compacts are studied by the discrete element methods (DEM). In DEM, the particulate nature of the powder is intrinsically taken into account by modeling each particle. The powders that we are interested in are modeled at the length scale of crystallites by building aggregates of spherical particles that are strongly bonded together. The simulations allow the green strength to be related to the crystallite size and to the amount of aggregate breakage during compaction. DEM simulations also provide fracture and yield surfaces which may be used in Finite Element simulations for complex stress states. More generally, DEM allows a better understanding of the densification mechanisms (i.e. fracture and/or rearrangement of the particles).

CA-4:L10 Reactive Spark Plasma Sintering of Si3N4/SiC Composites

Z. TASLICUKUR[1], F. Cinar Sahin[2], N. Kuskonmaz[1], [1]Yildiz Technical University, Metallurgical and Matls Engrg Dept., Istanbul, Turkey; [2]Istanbul Technical University, Metallurgical and Matls Eng. Dept., Istanbul, Turkey

Si3N4/SiC composites containing different amounts of SiC were produced by reactive spark plasma sintering of Si3N4, SiO2 and C black. Y2O3 and AlN were added as sintering additives. The SPS process was carried out at sintering temperature of 1650 0C for 5 min with uniaxial pressure of 40 MPa in a nitrogen atmosphere.The mechanic properties and morphology of Si3N4 ceramic composite were determined. Microstructures of the sintered samples were observed by SEM images and phase compositions were analysed by XRD.

CA-4:L11 Monitoring Constrained Sintering of Yttria Stabilised Zirconia Coatings Using Fluorescence Spectroscopy

Ian P. Shapiro*, Ping Xiao, University of Manchester, Manchester, UK

The constrained sintering behaviour, in particular density and residual stress within yttria stabilised zirconia (YSZ) coatings has been investigated. Coatings were produced using electrophoretic deposition on both Fecralloy and gold coated YSZ substrates and sintered in air at 1100 °C and 1200 °C. Coatings contained 1 wt. % alumina which, in conjunction with fluorescence spectroscopy, can monitor residual stress. The residual stress within the alumina phase is linked to the coating density and the substrate constraint. Hence fluorescence spectroscopy can be used to monitor the coating density after sintering. The residual stress is also seen to vary for different substrates and substrate thicknesses. For rigid substrates the density across the coating is even, as expected from modelling literature.

CA-4:L12 Microstructural and Phenomenological Analysis of the Reaction Sintering of a Nickel Ferrite Based Cermet

G. Largiller*, C. Carry, D. Bouvard, Grenoble-INP, CNRS/UJF, SIMaP, St Martin d'Heres, France; A. Gabriel, Rio Tinto Alcan, CRV, Voreppe, France

This study presents two approaches of the reaction sintering of nickel ferrite based materials. In a first time, the microstuctural phenomena occurring during sintering are investigated. Nickel ferrite cermets are obtained by a classical powder metallurgy route starting from a mixture of NiFe204, NiO, including polyvinyl alcohol as a binder (PVA). The sintering of such mixture involves classical densification mechanisms at low temperature and is driven by a thermo chemical reaction at high temperature. The oxygen content of the mixture as well as the atmosphere play a role of paramount importance in the densification during the reaction sintering. In a second time, a phenomenological equation is used to describe the macroscopic behaviour of the material during sintering. This constitutive equation considers the material as a continuum and may enable one to predict the densification behaviour of a powder under different thermal treatments and the impact of compact geometry, external loading on strain and stress generation. The method used for the identification of the parameters is based on dilatometry measurement. A wide understanding of nickel ferrite cermet sintering is obtained by combining the microstructural analysis with the phenomenological approach hereby proposed.

CA-4:L15 Numerical Modelling and Experimental Characterization of the Pyroplasticity in Ceramic Materials During Sintering

P. Bene*, D. Bardaro, D. Bello and O. Manni, Consorzio Cetma, Brindisi, Italy

The aim of the work is the study of the pyroplasticity in ceramic materials in order to simulate the deformations of complex ceramic component during sintering. A ceramic material undergoing densification can be treated as a linear viscous material. The viscosity depends strongly on the relative density and temperature. Generally, the viscosity decreases as the temperature increases, however densification and the consequent grain growth, result in a viscosity increase. A bending creep test is proposed for measuring the change in viscosity of the ceramic material during densification. Equations, based on beam deflection theory, are derived to determine the viscosity during the whole firing cycle by measuring the deflection in the centre of a series of rectangular specimens. In addition, dilatometric analyses are performed to measure the sintering shrinkage and the specimen density, which continuously changes during the sintering process. On the basis of an accurate experimental characterization the parameters of Maxwell viscoelastic constitutive law are derived. Numerical codes are used to predict the pyroplastic deformations of complex ceramic components in order to optimize the mould design phases and to reduce the time to market of new ceramic shapes.

CA-4:IL17 Spark Plasma Sintering of Ceramics: From Practice to Modelling

Zhe Zhao, Dept. of Physical-Inorganic and Structural Chemistry, Stockholm University, Stockholm, Sweden

Although Spark Plasma Sintering (SPS) has become a popular sintering technique for ceramics, especially those difficult to sinter with other sintering methods, there are still several important issues to clarify: 1) are there any plasma exist in SPS? 2)are there any extra densification contribution from the electric field/current? 3)what's the reason for the controversial results from different groups? etc.. Here several general issues concerning the sintering mechanisms, carbon contamination, sample discoloration and homogeneity in microstructure are discussed in terms of both practical operation parameters and modelling analysis. The thermodynamic analysis with constant heating rate sintering experiments showed that there is no change in the controlling diffusion process in SPS, compared with conventional pressureless and pressure-assisted sintering. The enhanced densification is the result of increased active diffusion species other than changing diffusion path. By FEM analysis, it is confirmed that the intrinsic temperature and stress gradient in SPS process can't be eliminated absoluetly, but homogeneous microstructure can be realized by better powder processing and sintering parameter control, e.g. pressure profile and heating rate etc..

CA-4:IL18 Multi-physics Simulation of Sintering

Veena Tikare, Sandia National Laboratories, Albuquerque, NM, USA

Simulating the detailed evolution of microstructure at the mesoscale is increasingly being addressed by a number of methods. Discrete element modeling and Potts kinetic Monte Carlo have achieved success in capturing different aspects of sintering well. Discrete element cannot treat the details of neck formation and other shape evolution, especially when considering particles of arbitrary shapes. Potts kMC treats the micorstructural evolution very well, but cannot incorporate complex stress states that form especially during differential sintering. A model that is capable of simulating microstructural evolution during sintering at the mesoscale and can incorporate differential stresses is being developed. This multi-physics model that can treat both interfacial energies and the inter-particle stresses will be introduced. It will be applied to simulate microstructural evolution while resolving individual particles and the stresses that develop between them due to local shrinkage. Results will be presented and the future development of this model will be discussed.

CA-4:L21 Simultaneous Synthesis and Sintering of Al2O3/Mo2N Composites Using Capsule-free Nitrogen Hot Isostatic Pressing and their Characterization

Ken Hirota*, Katsuya Takaoka, Yasushi Murase, Masaki Kato, Department of Molecular Chemistry & Biochemistry, Faculty of Science & Engineering, Doshisha University, Kyo-Tanabe, Japan

Synthesis of dense composite materials with the compositions of Al2O3/Mo2N=100/0~40/60 vol% has been attempted directly from Al2O3/

Mo mixed raw powder compacts using capsule-free N2 hot isostatic pressing (HIP). During HIPing [1500 °C/(16~20-200MPa)/1h], solid/gas reaction between Mo and N2 was performed to form Mo2N. The most of sintered composites consisting of only Al2O3 and Mo2N phases reached relative density higher than 98.0% with closed pores nevertheless capsule-free HIPing. Distribution of Mo2N particles just formed suppressed the grain growth of Al2O3 during sintering. Mechanical properties, such as bending strength (σ), Vickers hardness (HV), fracture toughness (K1C), and other properties have been evaluated as a function of their compositions. The best mechanical values of σ (~573 MPa), HV (~20.3 GPa) and K1C (~ 5.00 MPa-m1/2) were attained at the composition of Al2O3/Mo2N=90/10 vol%, due to a high density (98.6%) and small grain size of Al2O3 matrix (Gs ~4.70 µm). Further addition of Mo2N reduced the sinterability of matrix grains, resulting in low densities of around 90% at the 40/60 vol% composition.

Session CA-5

Innovation in Processing Equipment and Technology

CA-5:IL01 **Rapid Prototyping of Lead-free Piezoceramics**

A. Dittmar, X. Tian, J.G. Heinrich*, Institute of Nonmetallic Materials, Clausthal University of Technology, Clausthal-Zellerfeld, Germany; W. Braue, German Aerospace Center, Cologne, Germany

Lead-free piezoelectric ceramics have gained popularity over lead-based ceramics owing to environmental concerns. In the present study K0.5Na0.5NbO3 (KNN) powder was used, prepared by calcination of pure carbonates and oxides at 900 °C, because of its high Curie point above 400 °C and good piezoelectric properties. In order to validate the laser sinter ability of KNN, a 100 Watt CO2 laser with a beam diameter of 0.6 mm had been used to densify the surface of KNN samples. Dense KNN layers with a thickness of 100-200 µm have been obtained. The influence of dense KNN layers on the piezoelectric properties has been carefully studied. Aqueous KNN slurries have been developed by optimizing the zeta potential and the rheological properties. Laser direct sintering by using layer-wise slurry deposition (LSD) has been adopted to fabricate KNN components with complex structures. The Relationships between process parameters and microstructures as well as piezoelectric properties of the KNN samples will be discussed.

CA-5:IL02 **Pulsed Electric Current Sintering of Electrical Discharge Machinable Ceramics**

J. Vleugels[1]*, O. Malek[1, 2], K. Vanmeensel[1], S. Huang[1], S. Ran[1], O. Van der Biest[1], B. Lauwers[2], K.U.Leuven, [1]Department of Metallurgy and Materials Engineering; [2]Department of Mechanical Engineering, Leuven, Belgium

Pulsed electric current sintering allows to densify most ceramics at high heating and cooling rates within very short times at elevated temperature, allowing to minimise grain growth. In order to fully explore the PECS potential, it is beneficial to flow the current through the powder compact by either using conductive powder or a powder compact that becomes conductive during densification. Although in-situ Joule heating of the powder compact allows very fast heating rates, it does not necessarily result in a homogeneous temperature distribution. The influence of the current flow on densification and the impact of electrical conductivity on the temperature distribution during PECS will be illustrated. The PECS technology at present is limited to the fabrication of simple geometrical components. Electrical Discharge Machining (EDM) on the contrary allows production of complex shapes, providing the ceramic has a minimum electrical conductivity. Although EDM has no mechanical impact, the thermal impact is high and the EDM parameters should be carefully selected in order to optimise surface quality and component strength. The case studies that will be presented are ZrB2-SiC and B4C-TiB2 composites and ZrO2-based ceramics with conductive phase additions for die, gear and stamping tool.

CA-5:L03 **The Rapid Automated Materials Synthesis Instrument (RAMSI): A High Throughput Combinatorial Robot for Nano-ceramics Discovery**

T. Lin*, S. Kellici, K. Gong, K. Thompson, J.A. Darr, University College London, London, UK

A high throughput combinatorial robot RAMSI (Rapid Automated Materials Synthesis Instrument) is developed for nanoceramics synthesis. It can produce nanoparticle libraries quickly, and is significant in rapid materials discovery and optimisation for potential applications to energy, environment, electronics etc. The robot has 3 motor-driven axes moving in X-Y-Z space and linking the sections: synthesis, cleanup and printing. Specifically, the synthesis section contains a High Throughput Continuous Hydrothermal (HiTCH) flow synthesis reactor, which reaches significant production capability of 48 tubes of 50mL samples in 8 hours. The control system is programmed with parallel operations and multi-task assignments, which is supported by the high throughput hardware design. Key strategies include intelligent supernatant detection, dot printing protocols and robot arm route schedule etc. The commissioning of RAMSI showed its high efficiency by producing a library of yttria doped with europium (Y2O3:Eu3+). In a totally 6 hours' experiment, 8 unique 100mL samples were synthesized, cleaned and printed into 96 dots. The dots were heat-treated and affixed into a wellplate, and then illuminated under UV light, with certain compositions and heat-treatments yielding bright red phosphors.

CA-5:IL04 **Fabrication and Anisotropic Properties of Highly Textured Ceramics by Colloidal Processing in a High Magnetic Field**

Yoshio Sakka*, Thoru S. Suzuki, Testuo Uchikoshi, National Institute for Materials Science (NIMS), Tsukuba, Japan

The controlled development of texture is one of the ways for effectively improving properties of ceramics. We have demonstrated the new processing of textured ceramics with a feeble magnetic susceptibility by colloidal processing in a high magnetic field and subsequent heating. To obtain the oriented materials, the following conditions are necessary: (1) the particle should be single crystal and well dispersed, (2) crystal structure should be non-cubic to yield an anisotropic magnetic susceptibility, (3) magnetic energy should be larger than thermal motion energy, (4) the viscosity of the suspension should be low enough to rotate the particles with a low energy, and (5) grain growth is necessary to obtain a highly oriented structure especially when spherical particles are used. Colloidal processing in a high magnetic field confers several advantages and it is possible for this type of processing to be applied to non-cubic ceramics, such as alpha-alumina, titania, zinc oxide, tin oxide, hydroxyapatite, aluminium nitride, silicon carbide, silicon nitride, etc. Also textured ceramics with complicated structure can be fabricated by reaction sintering, such as beta-alumina, SiC-mullite-alumina nanocomposite, beta-Si3N4, etc. Here, some anisotropic properties are demonstrated.

CA-5:IL05 **Thermoplastic Shaping - Advances in Extrusion Processes**

F.J. Clemens, M.R. Ismael, V.L. Bueno, Empa, Swiss Federal Laboratories for Materials Testing and Research, Dübendorf, Switzerland

High performance ceramics, often require the elimination of clay from extrusion formulations because of its chemical incompatibility with that of the desired ceramic materials. Therefore organic materials are frequently used in ceramic extrusion to provide plastic flow. Not only plastic behav-iour is important for the extrusion of ceramic bodies. There are many other characteristics which can be tailored by the suitable addition of organics in a ceramic extrusion paste. Nowadays, to evaluate the right extrusion composition of the ceramic pastes, an understanding of the rheological properties such as viscosity, extensional viscosity and wall slip is crucial. This could be done either by a special extrusion die or simply by investigating the properties by using a high pressure capillary rheometer. The presentation will give an overview about binder systems and their influence on the processability of the ceramic pastes. Using PZT and cellulose based feedstocks, the influence of the rheological properties to achieve a well defined co-extruded structure will be demonstrated. Co-extruded, monofilament composites or hollow fibre structures with well preserved fibre morphologies and defined interfaces between the co-extruded materials could be achieved.

CA-5:IL06 **Rapid Prototyping of Complex Ceramic Forms**

N. Travitzky, Department of Materials Science, Glass and Ceramics, University of Erlangen-Nuremberg, Erlangen, Germany

Design and development of advanced materials for medical and high performance applications ranging from automotive to aerospace and bringing these materials into use is one of the most challenging tasks of modern materials engineering. Ceramic materials are natural candidates for these demanding applications. Owing to the inability of current technology related methods to produce complex-shaped ceramic parts with the desired microstructures and properties, novel techniques, so-called Solid Free Form (SFF) or Rapid Prototyping (RP) are becoming increasingly important processes. The mechanical properties of the materials fabricated by Rapid Prototyping techniques in many cases are similar to the corresponding properties for commercially available ceramic-based materials fabricated by other methods. RP technologies can create parts using advanced materials superior to traditional ones. Layer-wise fabrication of the parts by RP techniques, however, can lead to unsatisfactory surface roughness. In order to improve the surface finish different methods have been studied. Dense ceramic/glass, porous ceramics and ceramic/metal composites with complex geometry have been fabricated via different RP processing routes. Microstructure and mechanical properties of the fabricated composites have been investigated.

Poster Presentations

CA:P01 **Effects of Aging on the Characteristics of Nd:YAG Nano-powders**

Xiaolin Zhang*, Duo Liu, Hong Liu, Jiyang Wang, State Key Laboratory of Crystal Materials, Shandong University, Jinan, Shandong, P.R. China

Yttrium aluminum garnet nano-powders doped with neodymium (Nd:YAG) were synthesized by the microwave homogeneous precipitation method using Al(NO3)3.9H2O and Y(NO3)3 as mother salt, and urea as precipitant. Effects of different aging conditions which affected the synthesis of Nd:YAG nano-powders, were analyzed and discussed. Our results show that Nd:YAG precursors and Nd:YAG nano-powders were affected remarkably by different aging conditions. Effects of aging at the closed state were better than that at the open state, Nd:YAG nano-powders with uniform-size and approximately elliptical grains could be easily produced by aging at the closed state, and effects of aging were sensitive to the outer environment. The average diameter of Nd:YAG nano-powders obtained by aging at the closed state for six days was remarkably smaller than that obtained by aging at the closed state for different time. In addition, Nd:YAG nano-powders with good sinterability could be obtained by aging at the closed state for six days, the transmittance of Nd:YAG ceramic sintered under vacuum at 1730 °C for 10h was close to 75%.

CA:P02 **Elaboration and Mechanical Characterization of Al2O3-ZrO2-YAG Ultra-fine Composites**

Paola Palmero, Valentina Naglieri, Giulia Spina*, Laura Montanaro, Dept. of Materials Science and Chemical Engineering, Politecnico di Torino, LINCE lab., INSTM PoliTO R.U., Torino, Italy

The design of engineered ceramics has changed from microstructures to nanostructures in the last few years, since improved mechanical properties were proven in nanomaterials. When nanocomposites are concerned, the design of possible nano/micro-structures can be further extended, offering new challenges for both functional and mechanical applications. In this paper, Al2O3-YAG-ZrO2 composites, with ultra-fine microstructures are developed. The composite powders are produced by surface modification of a commercial nano-crystalline alumina powder with inorganic precursors of the desired second phases. The doped powders are calcined at various temperatures and for different times: as a function of the thermal treatment, zirconia directly crystallizes on the alumina surface, while YAG phase is yielded by solid state reaction among an amorphous yttrium-rich precursor and the alumina powder. Several compositions, with increasing second phases volume fractions are investigated. Precisely, from Alumina-5vol.%YAG-5vol.%ZrO2 (AYZ-5) to Alumina-33vol.%YAG-33vol.%ZrO2 (AYZ-33). The role of the second phases amount on the microstructural features and on some mechanical data preliminary evaluated (such as hardness and fracture toughness) is established.

CA:P03 **Effects of Firing Temperature and Time on the Luminescency of Phosphors in the Strontium Aluminate System Co-doped by Eu2O3 and Dy2O3 and Prepared by Solid State Reaction Processing**

Selvin Yesilay Kaya, Anadolu University, Faculty of Fine Arts, Dept. of Glass, Eskisehir, Turkiye; Bekir Karasu, Anadolu University, Faculty of Eng. and Architecture, Dept. of Materials Science and Eng., Eskisehir, Turkiye; Guray Kaya, Dumlupinar University, Faculty of Eng., Dept. of Ceramic Eng., Kutahya, Turkiye; Erkul Karacaoglu*, Anadolu University, Faculty of Eng. and Architecture, Dept. of Materials Science and Eng., Eskisehir, Turkiye

In this study photoluminescency and crystallisation during sintering were examined as functions of sintering time and temperature in reducing atmosphere. Long afterglow phosphors in strontium aluminate system doped with Eu+3 and Dy+3 were synthesized at different firing temperature for various time. X-ray diffraction was employed to characterize the crystal phases of phosphors. Scanning electron microscopy (SEM) investigations were carried out to understand surface morphology. The optical properties of the phosphors have been investigated by Phosphorescence Spectrophotometer. The changes in emission and excitation spectrum were discussed accounting firing time and temperature.

CA:P04 **Influence of Eu+3 and Dy+3 Contents on the Properties of Long Afterglow Strontium Aluminate Phosphors**

Selvin Kaya Yesilay*, Anadolu University, Dept. of Glass, Faculty of Fine Arts, Eskisehir, Turkiye; Bekir Karasu, Anadolu University, Dept. of Materials Science and Engineering, Faculty of Engineering and Architecture, Eskisehir, Turkiye; Guray Kaya, Dumlupinar University, Ceramic Engineering, Faculty of Engineering, Kutahya, Turkiye

The detailed preparation process of Eu2+ and Dy3+ ion co-doped phosphor powders in strontium aluminate system with bluish-green long afterglow by solid state reaction method in the reducing atmosphere is reported. X-ray diffraction, scanning electron microscopy, X-ray flurorescence and grain size analysis were made to determine the effects of amount of Eu and Dy ions on the luminescent properties of the synthesized phosphors. Moreover, luminescence properties were determined by measuring the photoluminescence spectra. The maximum emission intensity of these phosphors under excitation was investigated. The results indicated that the main peaks in the emission spectrum and the excitation spectrum shifted to the long wavelength by increasing Eu-Dy mol percent.

CA:P05 **Glycine-nitrate Synthesis of Sr Doped La2Zr2O7 Pyrochlore Powder**

Yan Chen*, Nina Orlovskaya, Dept. of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL, USA; Nicholas Miller, Harry Abernathy, Daniel Haynes, David Tucker, Randall Gemmen, U.S. Dept. of Energy National Energy Technology Lab., USA

The oxides with A2B2O7 (pyrochlore) structures have received significant attention as materials for use in powder generation, heating elements, oxygen electrodes, solid electrolytes for solid oxide fuel cells (SOFC's), thermal barrier coating, and for multiple electronic applications. Different techniques, such as solid state synthesis, sol-gel and combustion, have been employed for producing La2Zr2O7 (pyrochlore) powders. One of the unique synthesis routes for powders is the glycine-nitrate combustion method, which shows superior properties of the synthesized powder by using glycine as a complexing agent. Here we report an application of the glycine-nitrate combustion method for the synthesis of Sr doped La2Zr2O7 (pyrochlore) powders. Selected characteristics of the synthesized powders, such as lattice parameters and crystallite size by XRD, the vibrational response by Raman spectroscopy, the morphology of the particles by SEM and TEM, along with the specific surface area and particle size have been investigated.

CA:P08 **Synthesis of Gadolinium Oxynitride with Cuspidine Structure and its Luminescence Properties**

Sakurako Mihara*, K. Yamaguchi, S. Koda, K. Itatani, Sophia University, Tokyo, Japan; H.T. Hintzen, A.C.A. Delsing, Eindhoven University of Technology, Eindhoven, The Netherlands

We studied the preparation conditions of rare-earth doped Gd4Si2O7N2 and evaluated its luminescence properties. The starting materials of a-Si3N4 and Gd2O3 were stoichiometrically weighed and then mixed with 1 mol% rare-earth oxide (activator). The mixtures doped with Ce3+, Sm3+ and Tb3+ were heated at 1600 ºC for 2 h in N2 atmosphere; only Gd4Si2O7N2 was detected from the resulting powder. Then the near-ultraviolet light with the wavelength of 370 nm was irradiated to the resulting compounds. The blue light was emitted by doping 1 mol% Ce3+ to Gd4Si2O7N2 (the excitation and emission peaks at 390 nm and 448 nm (blue light emitting), respectively); the relative emission intensity (REI) was 0.182 (standard substance: YAG: Ce3+ (P46-Y3)). When 1 mol% Sm3+ was doped to Gd4Si2O7N2, the emission peak appeared at 603 nm (excitation peak: 296 nm) where the orange light was emitted (REI = 0.136). Furthermore, when 1 mol% Tb3+ was doped to Gd4Si2O7N2, the emission peak appeared 545 nm (excitation peak: 246 nm) where the green light was emitted (REI = 0.455). Overall, the doping of Ce3+, Sm3+ and Tb3+ to the Gd4Si2O7N2 contributed to emitting the lights with blue, orange and green colors.

CA:P09 **The Isothermal and Non-isothermal Crystallization Kinetics of La2O3 Doped, Sol-gel Derived Mullite**

V. Mandic*, E. Tkalcec, S. Kurajica, University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia

Nucleation and growth of mullite in Al2O3-SiO2 monophasic gels with constant molar ratio Al/Si=3:1 doped with 4.76, 9.09 and 13.04 mol% La2O3 was investigated using differential-thermal analysis (DTA), differential-scanning calorimetry (DSC), X-ray diffraction (XRD), and scanning electron microscopy (SEM). DTA analysis showed that the temperature range of mullite crystallization is enlarged, while the temperature of maximum crystallization rate is shifted to higher temperatures (from 983 °C to 988 °C) as a result of lanthania doping. Kinetic parameters such as activation energy, Avrami exponent and frequency factor have been simultaneously calculated from DSC data using isothermal and non-isothermal kinetics model. It has been established that crystallization kinetic parameters are in correlation to the doping level. Activation energy of mullite crystallization decreases with La2O3 doping level. The quantity of mullite phase in the ceramics decreases on account of α-Al2O3 crystallization with La2O3 content. The densification of sintered bodies was improved by La2O3. The mullitization behavior was attributed to the formation of the low-viscosity liquid phase due to addition of dopant.

CA:P10 **Piezoelectric Lead Free Ceramics in the Solid Solution KNN**

R. López, M.E. Villafuerte-Castrejón*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México D.F., México; F. González, Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, México D.F., México; A.M. González, Grupo Poemma, Technical University of Madrid, EUIT Telecomunicación, Madrid, Spain

In recent years lead free ceramics have been deeply studied, meanly the solid solution formed in the system $KNbO_3$-$NaNbO_3$ with the stoichiometric composition $K_{0.5}Na_{0.5}NbO_3$ (KNN). Only a few synthesis routes, besides the conventional solid state method, as sol-gel and Pechini have been reported. It is necessary, in order to preserve the stoichiometry of the lead free ceramic, to find an alternative route of synthesis which avoids long heat treatments at high temperature. By spray-drying technique the compounds $K_{0.5}Na_{0.5}NbO_3$ (KNN), $(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}NbO_3$ (KNLN) and $(K_{0.48}Na_{0.52})_{0.96}Li_{0.04}Nb_{0.85}Ta_{0.15}O_3$ (KNLNT) were synthesized and their piezoelectric properties were measured. For composition KNLNT, the values of k_p, d_{31}, tan δ, $2P_r$ and $2E_C$ are 0.42, 59 (pC/N), 0.01, 25.98 ($\mu C/cm^2$) y 25.73 (kV/cm).

CA:P11 **Production of Foundry Filters Using Alumina from the Aluminum Anodizing Process**

G.G. Moraes[1], B.G. Oliveira[2], C. Siligardi[3], D. Sighinolfi[4], M.D.M. Innocentini[5], A.A. Martins de Oliveira Jr.[1], D. Hotza[1], A.P. Novaes de Oliveira[1]*, [1]Federal University of Santa Catarina (UFSC), Florianópolis (SC), Brazil; [2]University of the Joinville Region (UNIVILLE), Joinville (SC), Brazil; [3]University ofi Modena and Reggio Emilia (UNIMORE), Modena, Italy; [4]Expert System Solutions S.r.l., Advanced Laboratory Equipment, Modena, Italy; [5]University of Ribeirão Preto, São Carlos - SP, Brazil

The manufacturing and materials transformation industries generate, to a greater or lesser extent, amounts of residues, which do not always have an adequate ecological destination. In many cases, however, these secondary products can be directly re-used as raw materials in other industrial processes. In this context, this article presents the characterization of the sludge generated in the aluminum anodizing process and emphasizes the application potential of this residue as a raw material for the production of industrial ceramic filters. Results show that the high alumina contents (89-97 wt%) and composition constancy, as well as the low particle size (~1 mm) after calcination, render this residue a suitable raw material to produce alumina filters with optimized properties for filtration and so purification of liquid metals to cast engineering components with higher performance.

CA:P15 **On the Hydrothermal Synthesis of xCr2O3-(1-x)Fe2O3 Nanoparticle System**

L. Diamandescu*, D. Tarabasanu-Mihaila, F. Vasiliu, M. Feder, I. Mercioniu, T. Popescu, National Institute of Materials Physics, Bucharest, Romania

A tentative to prepare solid solutions based on isostructural oxides Cr2O3 and Fe2O3 by a hydrothermal route at moderate temperature is presented. Mixtures of Cr(OH)3 and Fe(OH)3 hydroxides, obtained from the corresponding chlorides by precipitation with ammonium hydroxide solution, were used for the hydrothermal synthesis at 200 °C. The XRD, TEM and Mössbauer spectroscopy investigations evidenced the synthesis of solid solution up to $x=0.2$. At higher chromium contents, amorphous phases consisting in iron and chromium hydrates are formed. After a thermal treatment at 600 °C, the solid solutions appeared up to $x=0.3$. A separate phase crystallization (Cr:Fe2O3 and respectively Fe:Cr2O3) was evidenced in the range of $x=0.4$-0.9. At $x=1$ pure nanoscaled (~19 nm) Cr2O3 phase was obtained. Therefore, even the hydrothermal route is able to synthesise solid solutions only at low chromium content ($x \leq 0.2$), the pure or low iron doped Cr2O3 nanoscaled phase can be obtained simply by a hydrothermal route at 200 °C followed by thermal treatment at 600 °C.

CA:P16 **Synthesis of High Purity Fine B4C Powders via the Sol Gel Process**

H. Sinaei Pour Fard*, H.R. Baharvandi, Faculty of Materials and Manufacturing Process, MUT, Tehran, Iran

Fine B4C powders have been synthesized at 1350-1500 °C by the sol gel process using boric acid and citric acid as the starting materials. B/C molar ratio of the starting materials is ascertained, thermodynamics temperature of the reactions is calculated and the effect of precursors ratio is discussed. The experimental results indicate that the best boric acid to citric acid molar ratio is 2.2 to reach high purity boron carbide powders with less than 2.3 free carbon contents. XRD and PSA results show that using molar ratio of 1.6 of precursors and decreasing the pyrolizing time to 2.5 hrs at 1450 °C results more uniform particles with $D90=2.91\mu m$.

CA:P17 **Preparation and Characterization of New Oxyfluoride Phases (Ba,Na)(Ti,Mg)(O,F)**

D. Talantikite-Touati*, Dept. of Chemistry, Abderrahmane Mira University, Bejaia, Algeria; L. Benziada, Faculty of Chemistry, USTHB,El-Alia, Bab-Ezzouar, Algiers, Algeria

The perovskite materials ABO3 are in huge expansion worldwide since the discovery of ferroelectricity in BaTiO3 ceramic. The barium titanate is one of the most widely used dielectric material. It has been utilized as primary material for multi-layer ceramic capacitors (MLCC), but then, it has a numerous applications in electro-optic devices, thermistors, ultrasonic transducers and in the memory industry because of its good dielectric characteristics. Pure BaTiO3 exhibits a phase transition at 120 °C and its dielectric constant can achieve 2000 at room temperature. However, the dielectric properties could have improved using a various dopants. The Barium titanate BaTiO3 is initially synthesized in air by solid state reaction, at 1100 °C from an homogeneous mixture of Barium carbonate (BaCO3) and titanium dioxide (TiO2). Oxyfluoride phases have been synthesized in free atmosphere, using the BaTiO3 perovskite and the fluorides NaF and MgF2. This powder mixture is finely milled for 1 hour in an agate grinder and disc tablets of 13mm diameter and about 1mm thickness are prepared by cold isostatic pressing. The pellets are sintered in free atmosphere at 950 °C during 4 hours. The purity of BaTiO3 and oxyfluorides has been checked by X-Ray diffraction (XRD). The crystalline parameters have been determined then refined by the least square method. The phase transitions in these new phases have been investigated by dielectric measurements and differential scanning calorimetry (DSC).

CA:P20 **Synthesis of Scandium Oxide Nanopowders by the Sol-gel Route**

N. Poirot, LEMA, UMR 6157, CNRS-CEA, IUT de Blois, Blois cedex, France; P. Boy, Laboratoire Sol Gel, CEA/Le Ripault, Monts, France; C. Autret-Lambert, LEMA, UMR 6157, CNRS-CEA, Parc Grandmont UFR Sciences, Tours, France; P. Belleville*, L. Bianchi, Laboratoire Sol Gel, CEA/Le Ripault, Monts, France

The main objective of this work is to prepare oxohydroxide nanoparticles by a sol-gel route with controlled size and shape and then annealed at higher temperature to obtain scandium oxide Sc2O3. The sol-gel process allows the preparation of oxide nanoparticles directly in solution, without additives. Good oxide homogeneity, high purity, shape and size control are some advantages of solution process. The precursor used is ScCl3. ScOOH is produced by precipitation with NaOH and reflux at 100°C at constant volume. In this condition, no hydrothermal process is necessary, only pH control and reflux time duration are required. Furthermore, the salt elimination is processed by water dialysis leading to obtain a stable pure ScOOH sol depending on pH and reflux time duration. Finally the influence of pH and time preparation on the ScOOH size and shape is clearly put into evidence as well as the impact of ScOOH preparation conditions on final Sc2O3 features.

CA:P23 **Description of Carbides Sintering Process using Kuczynski and Frenkel Sintering Models**

A. Gubernat, AGH-University of Science and Technology, Faculty of Materials Science and Ceramics, Cracow, Poland

In this work sintering kinetics of some pure i.e. without Co, Ni or Fe additions metal-like carbides such as TiC08, NbC, WC were studied. Measurements were made by means of a high temperature dilatometer. Sintering shrinkage as a function of time was recorded under isothermal conditions. An analysis of the sintering kinetics was based on sintering models worked out by Kuczynski and Frenkel. Kinetic equations describing a sintering process of each carbide were formulated according to the Kuczynski's model. Comparison of kinetic equations and densification behaviour was fundamental to determine similarities and differences in the sintering process of the studied carbides. The second sintering model was used to determine sintering parameters i.e. initial shrinkage rate, the limit of shrinkage at infinite time and initial apparent viscosity as a function of temperature. Results of the investigations allowed to obtain full sintering characteristics of the studied metal-like carbides.

CA:P25 Effect of the Two-steps Sintering in the Microstructure of Ultrafine Alumina

A.S.A. Chinelatto*, M.K. Manosso, A.L. Chinelatto, UEPG, Ponta Grossa, PR, Brazil; E.M.J.A. Pallone, USP-FZEA, Pirassununga, SP, Brazil

The control of the heating curve to manipulate microstructure during sintering is a way that has being studied and it presents advantages such as simplicity and economy. In this work, it was studied the sintering in two-steps of a commercial ultrafine alumina. For this, the alumina powder was deagglomerated in milling ball and the specimens for sintering were pressed. Sintering was performed in a dilatometer, with constant heating rate of 15 °C/min up to 1500 °C. By these results, heat treatment temperatures for two-step sintering were defined. The sintering specimens were characterized through the apparent density measures using Archimedes method, the grain size measures using image analysis program and microstructural analysis using a scanning electron microscope. The results showed that the two-step sintering influence in the development of the final microstructure and permit the control of the grain size and density.

CA:P26 Densification Study of HA-Mg Samples Synthesized with Ultrasound

D.S. Gouveia, A.H.A. Bressiani, J.C. Bressiani*, Materials Technology and Science Center - CCTM, Institute of Energetics and Nuclear Research - IPEN, Cidade Universitária, São Paulo-SP, Brazil

In this work the Hydroxyapatite (HA) densification was investigated in samples prepared by the neutralization method with or without ultrasonic technique and with different amount of magnesium (0.0, 0.36 and 0.49 wt% of Mg2+). The as-prepared and calcined at 800 °C/3h powders were characterized by X-ray diffraction (XRD) technique, specific surface area (BET) and transmission electron microscopy (TEM). HA powders were isostaticaly pressed at 200MPa into pellets and sintered in air at 1100ºC/1h. The density of the sintered samples was determined by Archimedes' Method using distilled water. The relative density was obtained by taking the theoretical density of hydroxyapatite, 3.156 g/cm3. The crystalline phases present in the samples were identified by XRD. The microstructural evolution for the samples was examined using scanning electron micrographs (SEM). The shrinkage of the green compacts was measured in function of temperature by dilatometry (Setaram-SETSYS 16/18), from room temperature up to 1250 °C/15min at a constant heating rate (10 °C/min). The neutralization method associated with the ultrasound technique and magnesium addition was effective in the synthesis of hydroxyapatite nanopowders. However the density of these powders were strongly influenced due to the phases change

CA:P27 Enhanced Densification and Grain-size Refinement in Cation-doped Tetragonal Zirconia

K. Hiraga*, H. Yoshida, K. Morita, B.-N. Kim, National Institute for Materials Science, Tsukuba, Ibaraki, Japan

The suppression of the grain growth during the final stage of densification is generally difficult, since the driving forces for densification and grain growth are comparable. This relationship may, however, be altered by doping of some cations that segregate along grain-boundaries. The segregation may simultaneously influence grain-boundary mobility through dragging and grain-boundary diffusion. This point was investigated in 3-mol%-yttria-stabilized tetragonal zirconia (3Y-TZP). The specimens used were cold-isostatically-pressed compacts of high-purity 3Y-TZP powders doped with 0.5 mol% divalent, trivalent and tetravalent cations. For an initial relative density of 52% and a sintering temperature of 1350 °C in air, the effects of doped cations were similar to each other in the enhancement of densification, but different in grain growth during densification. Some cations enhanced grain growth, whereas others tended to suppress grain growth in a final stage of densification where the density exceeds ~85%. The doping of the latter cations accordingly brought about a grain size finer than that of the undoped 3Y-TZP for a given relative density. It was also found that the grain-size refinement by the doping is enhanced by a two-step sintering method.

CA:P28 Synthesis and Sintering of Mullite Ceramics Using Microwave Heating

T. Ebadzadeh*, H. Barzegar-Bafroei, Ceramic Division, Materials & Energy Research Centre, Tehran, Iran

Mullite ceramics have been known as the engineering materials due to their special properties such as high refractoriness, good thermal shock resistance, low thermal expansion, good strength at low and high temperatures, good creep resistance and low dielectric constant. In this work, mullite samples were prepared by reaction sintering of alumina and silica gel and subsequent sintering in a microwave process. The sintering of samples was carried out at temperatures in the range of 1400-1500 °C with no soaking time. Density and porosity measurements showed a high density (89.3% TD) and low porosity (5.8%) for samples sintered at 1400 °C under microwave conditions while for samples sintered conventionally at this temperature for 2h, density decreased (81.9% TD) and porosity increased (18.5%). By increasing sintering temperature to 1450 and 1500 °C under microwave conditions, density increased (93.3 and 93.8% TD) and porosity decreased (0.31 and 0.36%), respectively. Microhardness measurements showed 27.6% increment when sintering temperature increased from 1400 to 1500 °C. The mean grain size increased (34.8%) for samples sintered in furnace rather than those sintered in microwave process.

CA:P29 Low-temperature Sintering of Apatite-type Lanthanum Silicate with Fluoride Additives

J. Takahashi*, H. Honda, T. Akashi, Graduate School of Engineering, Hokkaido University, Sapporo, Japan; H. Itoh, Department of Materials Science, Kitami Institute of Technology, Kitami, Japan; M. Kishi, Department of Mechanical Systems Engineering, Hokkaido Institute of Technology, Sapporo, Japan

Apatite-type lanthanum silicates are promising candidates for SOFC electrolytes at an intermediate temperature region (600-800 °C). However, high temperature (above 1500 °C) and prolonged sintering is required to obtain densified products. Therefore, it is desirable that a ceramic processing enabling accelerated mass transport at temperatures as low as possible is developed. One approach leading to low-temperature sintering is to utilize a liquid phase formed during sintering. In this study, various fluorides (3-8 mass%) were added to a La9.33Si6O26 (LSO) powder synthesized by solid state reaction of the corresponding oxides and the sintering characteristics of the fluoride-added LSO were examined in the temperature range of 1350 - 1450 °C in air to find out the appropriate additive(s) which can lead to the densification and controlled microstructure in low-temperature sintering. The addition of BaF2, AlF3, and Ba3Al2F12 (5 mass%) resulted in a substantial increase in bulk density of LSO samples after sintering at 1450 °C for 2h. The addition of BaF2 caused the enhanced ion conductivity of the LSO sample, which would be due to accelerated diffusion of the oxide ion by the incorporation of larger-sized Ba2+ into the La3+-site in addition to improved densification.

CA:P32 Processes of Phase-formation in the Solid State Synthesis of Ferrite Garnets

T.S. Livshits, IGEM RAS, Moscow, Russia

Ferrites with garnet-type structure (Ia3d) are considered as hosts for An and REE-containing high level wastes. It is important to realize an industrial scale method of synthesis of these phases. One of these methods is cold pressing and sintering. Two systems with bulk compositions of garnets Ca1.5GdCe0.5ZrFe4O12 and Ca2.5Ce0.5Zr2Fe3O12 were investigated to determine the optimum parameters for garnet formation. Ce4+ was used as surrogate of (Pu,Np)4+, Gd3+ replaced (Am,Cm)3+ and REEs. Samples were formed by pressing (25 C, 10-20 MPa) of homogenized oxide mixtures and sintering at 1100-1300 C for 1-20 hours. Two intermediate and final equilibrium stages of garnet formation are distinguished. Intermediate stages are observed at 1100 and 1200 C. Ceramics are characterized by polyphase structure, high porosity, low density. Samples in both systems consist of garnet, perovskite, Fe2O3 and ZrO2. Equilibrium is achieved at 1300 C for 1-3 hours heating. Ferrite garnets which contain up to 30 wt.% of CeO2+Gd2O3, are the main phases in all ceramics. There are small amount of perovskite in the samples. Thus cold pressing and sintering is an appropriate method of synthesis of garnet matrices.

CA:P33 Alumina - Zirconia Ceramics Synthesized via Aluminum Oxidation

S.N. Paranin*, V.V. Ivanov, S.V. Zayats, V.R. Khrustov, A.V. Spirin, S.Yu. Ivin, A.S. Kaygorodov, V.I. Krutikov, Yu.N. Koroleva, V.P. Loznukho, R.D. Nevmyvako Institute of Electrophysics, Russian Academy of Sciences, Ekaterinburg, Russia

Fabrication route and mechanical properties of alumina - zirconia ceramic composite are presented. Three types of non-agglomerated powders: alumina, passivated aluminum and zirconia with average particles sizes less than 150 nm were mixed, compacted and sintered in the air. Presence of a metal component at a composite powder allowed essentially to lower compaction pressure and simultaneously to provide high mechanical solidity of compacts for their machining. During following reaction sintering metal component was oxidized. Consideration has been given to influence of initial powders properties (morphology, phase composition, average size of particles), powder mixture composition and technological parameters (conditions of mixing, compressing and high-temperature processing) on structure, density and mechanical properties of ceramics.

CA:P34 **A New Powder Filler, Obtained by Applying a New Technology for Fly Ash Inertisation Procedure**

E. Bontempi*, A. Zacco, L. Borgese, A. Gianoncelli, L.E. Depero, Chemistry for Technologies Laboratory, University of Brescia, Brescia, Italy

In the last years several projects have been developed for treatment of fly ash with the aim of their reuse. A final target of these researches is to evaluate the real performance of the new materials obtained by the treatment and the actual and, if the case, potential markets for the foreseen products. Indeed, the use of a recycled inert would reduce the consumption of natural resources and this is one of the main environmental EU target. Examples are clinkering, road asphaltation and some construction work where specific performances are requested. Moreover, the reuse of inerted fly ash will obtain a reduction of carbon dioxide produced by the necessary treatments of primary materials, as limestone in concrete production. At the University of Brescia (Italy) a new process, based on colloidal silica medium, has been developed to inertise fly ashes, containing heavy metals. This approach appears to be quite promising for industrial application in view of the easiness that can be foreseen in applying it to existing plants treating industrial fly ash. The obtained inert product is a powder, that can be employed as a filler in several application. In this work we present first results about characterisation of this new powder material, that can be applied as a filler.

CA:P35 **Elastic Modulus and Hardness of CaTiO3, CaCu3Ti4O12 and CaTiO3.CaCu3Ti4O12**

M.A. Ramírez[1]*, R. Parra[2], M.M. Reboredo[2], J.A. Varela[1], M.S. Castro[2], L. Ramajo[2], [1]Chemistry Institute of São Paulo State University (UNESP), Bairro Quitandinha, Araraquara, Brazil; [2]Institute of Research in Material Science and Technology (INTEMA) (CONICET - University of Mar del Plata), (B7608FDQ) Mar del Plata, Argentina

The mechanical properties of three systems CaTiO3 (CTO), CaCu3Ti4O12 (CCTO) and intermediate nonstoichiometric CaTiO3.CaCu3Ti4O12 (CTO.CCTO) were investigated. The ceramics were sintered at 1100 °C for 180 min. The structure and surface morphology were investigated by XRD, SEM and elastic modulus and hardness of the surfaces by instrumented indentation. It was observed that CCTO presented the higher mechanical properties (E = 206 GPa, hardness = 8,84 GPa) while CTO.CCTO showed intermediate properties between CTO and CCTO.

CA:P36 **Rheology Behavior of Yttria Aqueous Suspensions for the Impregnation Method**

S.C. Santos, C. Yamagata, S.R.H. Mello-Castanho*, Nuclear and Energy Research Institute - IPEN / Sao Paulo, SP, Brazil

Preparing ceramic suspensions is an important step in ceramic processing. In order to apply a near net shape technique as the impregnation method, high-solids suspension being able to cover the total surface of organic matrix with good adhesion is necessary. The aim of this work is to tailor yttria suspensions through a rheological study in order to produce yttria reticulated bodies with fine characteristics for incandescence applications such as gas bulbuls. So, this work concerned the study of the effects of some variables such as dispersant dosage, solid loads, pH and additives concentration on the rheological behavior of yttria aqueous suspensions to obtain fine yttria porous bodies. Flow curves with shearing rate interval from 0 to 1000s^{-1} showed that 1 wt% of dispersant was enough to gain the lowest viscosity value for 30 vol% yttria suspensions. The porous ceramics were carefully thermally treated seeing that burning off the organic structure matrix could induce sensible residual stresses and disrupt the ceramic network. Sintering at 1450 °C showed ceramics with fine structural stability and high porosity.

Symposium CB

NOVEL ROUTES FOR CERAMICS SYNTHESIS AND PROCESSING

Oral Presentations

Session CB-1
Soft Solution Processing

CB-1:IL01 **Soft Processing for Ceramics: Single-Step Fabrication of Nano-Structured Oxide Ceramics(Particles, Films, Integrated Layers and Patterns) from Solution without Firing**

Masahiro YOSHIMURA, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan

Since 1989 when we found a method to fabricate $BaTiO_3$ film on Ti substrate in a $Ba(OH)_2$ solution by Hydrothermal Electrochemical[HEC] method at low temperatures of 60-200 °C, we have proposed an innovative concept and technology, “Soft Processing” or “Soft Solution Processing,” which aims low energetic (=environmentally benign) fabrication of shaped, sized, located, and oriented ceramic materials in/from solutions. It can be regarded as one of bio-inspired processing, green processing, or eco-processing. When we have activated/stimulated interfacial reactions locally and/or moved the reaction point dynamically, we can get patterned ceramic films directly in and/or from solution without any firing, masking or etching. Those Direct Patterning methods differ from previous patterning methods which consist of multi-step processes, for example: (1) synthesis of particles of compounds or precursors,[When this synthesis is done in a solution it is called as ”Soft Chemistry”.] (2) dispersion of the particles into a liquid (“ink”), (3) patterning of the particles on a substrate by printing of the “ink”, (4) consolidation and/or fixing of the particles’ pattern by heating and/or firing at high temperatures. (5) Those processes would cause cracking and/or peeling of patterned films due to the shrinkage of printed powders by sintering during heating and/or firing. The notable feature of Direct Patterning is that each reactant reacts directly on site, at the interface with the substrate. Therefore, the chemical driving force of the reaction, A+B=AB, can be utilized not only for synthesis but also for crystallization and/or consolidation of the compound AB. It is rather contrasting to general patterning methods where thermal driving force of firing is mostly used for the consolidation of the particles. We have developed the Direct Patterning of CdS, PbS, and $CaWO_4$ on papers by ink-jet reaction method and $LiCoO_2$ by electrochemically activated interfacial reactions. Furthermore, we have succeeded to fabricate $BaTiO_3$ patterns on Ti by a laser beam scanning and carbon patterns on Si by a needle electrode scanning directly in solutions. Recent success in TiO_2 and CeO_2 patterns by Ink-jet deposition, where nano-particles are nucleated and grown successively on the surface of substrate thus become dense even below 300 °C, will be presented. Transparent films of several hundred nm thick can be oftained by 20 times of ink-jet scanning during 15-30 min. As a development of Hydrothermal Electrochemical[HEC] method,we have proposed a new strategy: ”Growing Integration Layer[GIL] method”,which can provide well-adhered integrated/graded layers: Titanate/TiOx/Ti or Titanate/TiOx/Ti-alloys and/or metallic glass(es) at RT-150 C in a solution. This [GIL] strategy can be applied for many areas of functional ceramics. In addition,our recent results on mono-dispersed nano-particles of CeO_2,$(Hf,Eu)O_{2-x}$,Fe_3O_4, etc. will be presented.

CB-1:IL02 Novel Hydrothermal Solution Routes of Advanced Nanomaterials and Nanoceramics Processing

K. Byrappa, DOS in Geology University of Mysore, Manasagangotri P.O., Mysore, India

Novel hydrothermal solution processing routes are becoming the most efficient routes in recent years for advanced nanomaterials processing including the hybrid nanomaterials. These novel solution routes include several variations in the hydrothermal technique such as conventional hydrothermal, solvothermal, supercritical hydrothermal, ammonothermal, glycothermal, carbonothermal, etc. The current trends in the hydrothermal solution processing of materials, the importance of solubility study, thermodynamic calculations and the role of surfactants and chelates have been discussed in detail with reference to the processing of advanced nanomaterials such as high melting oxides and metal oxide - organic hybrid nanomaterials. The hydrothermal synthesis of nanomaterials and nanoceramics of high melting carbon polymorphs, rare earth vanadates, metal oxides and their nanocomposites have been discussed with an emphasis on the control of size and morphology, and surface charge.

CB-1:IL03 Non-aqueous Sol-gel Routes to Metal Oxide Nanostructures

Nicola Pinna, Department of Chemistry, CICECO, University of Aveiro, Campus de Santiago, Aveiro, Portugal; World Class University (WCU) program of Chemical Convergence for Energy & Environment (C2E2), School of Chemical and Biological Engineering, College of Engineering, Seoul National University (SNU), Seoul, Korea

Nonaqueous sol-gel routes are elegant approaches for the synthesis of nanomaterials. Indeed, high quality pure inorganic nanocrystals, ordered hybrid organic-inorganic materials or thin films by atomic layer deposition (ALD) can be obtained. In this communication, after an introduction to nonaqueous sol-gel routes to inorganic nanocrystals and ordered hybrid organic-inorganic materials synthesized in surfactant-free system, we will concentrate on the deposition of thin films and coatings by ALD. The similarities and differences of the chemical processes taken place in solution and in ALD will be discussed.

CB-1:IL04 Liquid Phase Morphology Control of Metal Oxides in Aqueous Solutions

Yoshitake Masuda, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan

Liquid phase morphology control of metal oxides was realized in aqueous solutions to form various nanostructures. Stand-alone ZnO self-assembled films were, for instance, prepared using air-liquid interfaces. The ZnO films had sufficiently high strength to free-stand-alone and showed high c-axis orientation. The films can be pasted onto desired substrates. ZnO particles having a hexagonal cylinder shape, long ellipse shape or hexagonal symmetry radial whiskers were also prepared in aqueous solutions. The morphology was controlled by changing the supersaturation degree. Anatase TiO2 particles with high surface area of 270 m2/g were prepared at 50 °C. The particles were assemblies of nano TiO2 crystals covered with nanorelief surface structures. The crystals grew anisotropically along the c-axis to form acicular crystals. TiO2 films consisted of anisotropic acicular crystals were also prepared. The films showed high c-axis orientation. Liquid phase morphology control of metal oxides would contribute to development of science and technology of metal oxides.

Y. Masuda et al., Cryst Growth Des 8083(2009), 555(2009), 275(2008), 169(2008), 75(2006), Chem Mater 1057(2008), 1002(2007), 3484(2004), 2615(2004) 2469(2003), 1236(2002), 5006(2002), Adv Mater 841(2005), 1461(2004)

CB-1:IL05 Granulation by Spray Freeze Drying and Pressing of Nano YSZ Powders

Jon Binner*, Bala Vaidhyanathan, Ketharam Annapoorani, Bala Raghupathy, Department of Materials, Loughborough University, UK

The current interest in nanocrystalline ceramics, materials with mean grain sizes <100 nm, lies in the unique properties they are being found to possess as it becomes increasing possible to produce engineering components. The processing of nanocrystalline yttria doped zirconia powder has been investigated at Loughborough via a series of research projects each focusing on a different stage of the manufacturing route. This holistic approach helped to transfer the developments achieved in every stage of the manufacturing process to the next and resulted in the ability to form fully dense YSZ components whilst retaining the final grain size as small as 65 nm. This paper will focus first on the ability to granulate the powder using spray freeze drying, resulting in the production of a free-flowing and crushable powder for die pressing, and then on the results of the pressing trials themselves.

CB-1:IL06 New Synthesis Process of Li, Na and K Niobates from Metal Alkoxides

Yoko Suyama, Shimane University, Nishikawatsu, Matsue, Japan

Recently, lead-free dielectric materials have attracted much attention, and their R&D have been eagerly performed from the environmental points of view. Among them, lithium niobate (LiNbO3), sodium niobate (NaNbO3), potassium niobate (KNbO3) and their solid solutions have been attracted attention because of superior piezoelectrical, pyroelectrical and electrooptical properties. These niobates have been commonly synthesized via solid state reactions at high temperatures over 1273K. Although this method is simple, single-phase stoichiometric materials with a reproducible [alkali metal]/[Nb] ratio are difficult to obtain by solid state reactions, due to evaporation of alkali metal at high temperatures. Furthermore, the high-temperature synthesis results in the grain growth of the particles, leading to disadvantages for fabricating dense ceramics by sintering and resulting electrical devices required fine-tuning of the dielectric properties. Therefore, an alternative synthesis process has been required to obtain fine-grained materials with controlled chemical composition. We have developed a novel synthesis route to produce fine lithium niobate, sodium niobate, potassium niobate and their solid solutions by thermal decomposition of the constituent double metal alkoxides. According to this method, niobate nano-particles with homogeneous and controlled chemical composition and with high purity were obtained at relatively low temperature. The new synthesis process and the characteristics of the obtained niobates are described.

CB-1:IL07 Glycol-based Precursors in the Synthesis of Mesoscopically Organized and Porous Nanoparticles

Nicola Huesing, Ulm University / Inorganic Chemistry, Ulm, Germany

Advances in designing nanostructured non-silicate oxides/phosphates with well-defined composition in the 2-50 nm length scale play a vital role in manifold fields, e.g. heterogeneous catalysis or energy storage applications. Modified sol-gel routes with different precursors, catalysts and/or structure directing agents provide an excellent option to yield those desired materials. Diol- or polyol- modified precursors such as tetrakis(2-hydroxyethyl)silane or the corresponding transition metal analogues have some distinct advantages in sol-gel processes (no co-solvent, neutral/ acidic conditions/ no catalyst to start the reactions, and the diols/polyols show a very good compatibility with e.g. lyotropic phases). These advantages allow for processing under conditions that cannot be applied with commercially available alkoxide precursors and thus for the synthesis of materials with unique structures, hierarchies and morphologies, e.g. particles. In this presentation, the opportunities and the potential opened by the application of these modified precursors in materials synthesis are discussed.

CB-1:IL07b Novel Sol-gel Synthesis of LiMn2O4 and LiNixCo1-xO2 Powders

A. Deptula[1]*, W. Lada[1], T. Olczak[1], D. Wawszczak[1], M. Brykala[1], F. Zaza[2], K.C. Goretta[3], [1]Institute of Nuclear Chemistry and Technology (INCT), Warsaw, Poland; [2]Italian National Agency for New Technologies, Energy and Environment (ENEA), CR Casaccia, Rome, Italy; [3]Asian Office of Aerospace Research and Development, Tokyo, Japan

A modified complex sol-gel process was developed to synthesize LiMn2O4 and LiNixCo1-xO2 powders. Sols were prepared from 1.5 M of Mn2+ or 1 M of xNi2+ and (1-x)Co2+ acetates plus ascorbic acid aqueous solutions by alkalizing them with LiOH and NH4OH. The ascorbic acid was added to prevent precipitation in the precursor solutions. When the sols were concentrated to one-third of their initial volume under reduced pressure and then gelled by drying for 10 days, heat treatment to >700 °C was accompanied by foaming, violent self-ignition, and formation of substantial carbonates in the Ni-containing species. Significant improvement to the process and resulting powders was gained by modifying the gelation step. When gelation and drying were carried out under reduced total pressure, no foaming occurred and heating at rates that exceeded 300 °C/min induced self-ignition. The resulting products were determined to be nearly phase pure and carbonate free by thermogravimetric, differential thermal, X-ray, and infrared spectroscopy methods.

CB-1:L08 Morphology Control of Rutile, Brookite and Anatase Type Titanium Dioxide by Hydrothermal Treatment of Water Soluble Titanium Complexes

M. Kobayashi*, M. Kakihana, IMRAM, Tohoku University, Sendai, Japan; V. Petrykin, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech; K. Tomita, Tokai University, Hiratsuka, Japan

We succeeded in the selective synthesis and morphology control of rutile, brookite and anatase type titanium dioxide by hydrothermal treatments of novel water soluble titanium complexes, which are characterized as environmentally benign titanium sources. Rod-like rutile particles were obtained by the hydrothermal treatment of a water soluble Ti complex with glycolic acid (GA) as a ligand at 473 K for 24 h. The aspect ratio of the obtained particles increased with extra additions of GA. Moreover, multineedle particles could be synthesized in the presence of a large amount of GA. Brookite particles were obtained using aqueous solutions of a titanium citrate complex with excess amounts of ammonia. The aspect ratio of the obtained particles increased with the amount of added ammonia, and ribbon-like agglomerates were produced at higher ammonium concentrations. Single phase anatase particles with about 10 nm spherical shape could be obtained using the titanium citrate complex without any additives. On the other hand, spindle-like anatase particles were produced under a given hydrothermal condition using the titanium citrate complex with ethylenediamine (EDA) as an additive. With increasing of the additional EDA, the shape of the obtained particles changed from spindle to bipyramid.

CB-1:L09 Synthesis and Characterization of High Surface Area Zinc Oxide-carbon Composite

T. Yong-JIn Han, Marcus A. Worsley, Theodore F. Baumann, Joe H. Satcher Jr., Tammy Y. Olson*, Physical and Life Sciences Lawrence Livermore National Laboratory, Livermore, CA, USA

Zinc oxide (ZnO) is an important II-IV, n-type semiconductor material with a wide band gap of ÄEgap = 3.37 eV with an exciton-binding energy of 60 meV. It also possesses interesting optical properties (i.e. transparent conducting film) as well as piezoelectric properties. These novel properties of ZnO have lead to applications in UV-light emitting diodes, lasers, photovoltaic solar cells, gas sensors, and biosensors with a limited success. One of the factors contributing to the limited success of ZnO in the above-mentioned applications is the overall lack of control in their surface area, structures and the ability to mass produce these novel materials. Therefore, a successful synthesis of 3 dimensional arrays of ZnO with a high surface area with a well-defined morphology is of critical importance for significantly improving and potentially enabling of both novel and critical applications. In this presentation, we will discuss a successful synthesis of high surface area ZnO by using high surface area carbon aerogel as a scaffold in combination with a simple sol-gel process. The resulting composite materials possesses specific surface area of ca. ~ 1200 m2/g. We believe this to be the highest surface area materials of ZnO.

CB-1:L10 Synthesis of Alumina and Aluminium Nitride Layers on a Graphite Substrate via a Sol-gel Route

F. Fontaine*, R. Pailler, A. Guette, Laboratoire des Composites Thermostructuraux (LCTS), Université Bordeaux 1, Pessac, France

In this study, our objective is to deposit an alumina or an aluminium nitride layer on a turbostratic carbon substrate. The coatings are synthesized via a sol-gel route and heat treated to crystallise alumina to its a form or to proceed to the carbothermal nitridation of alumina. The literature does not describe the synthesis of such layers on carbon substrates. Several slurries were elaborated using various solvents and catalysts, and aluminium-tri-sec-butoxide as an aluminium precursor. The coating is obtained by dropping the substrate in the sol. After drying and pyrolysis, the amorphous alumina layer obtained has a thickness from 500nm to 1µm. The material is finally heat treated. Several treatment conditions were evaluated. A thermodynamical study of the Al-C-O-N system will be drawn, and the compositions of the synthesized sol-gels and heat treatment parameters will be detailed. Then, the layer's morphology and structure will be characterized thanks to backscattered electrons, EDX and XRD analyses. The impact of heat treatment parameters and the composition of the sol will be discussed. Experimental results will be compared to the theoretical thermodynamics.

CB-1:L11 Synthesis of Monodispersed Plate-like CeO2 Particles by Mild Solution Process

S. Yin*, Y. Minamidate, T. Sato, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan

Monodispersed plate-like CeO2 particles were successfully synthesized by a mild solution process followed by calcination in air at 400 degrees centigrade. During the solution processing, monodispersed orthorhombic single-crystal of plate-like Ce2(CO3)3.8H2O and CeOHCO3 were obtained by using Ce(NO3)3.6H2O as cerium source, and NaHCO3-NaCO3 mixed aqueous solution as precipitation reagent and carbon source. The pH value, which was precisely controlled by changing NaHCO3/NaCO3 molar ratio in the solution, affects the morphologies and phase composition of the cerium carbonate compounds. High pH values led to the formation of layered Ce2(CO3)3.8H2O, while low pH values preferred to CeOHCO3 formation. The additive of ethylene glycol in the solution decreased the particle size of the cerium carbonate effectively. The CeO2 particles synthesized by the decomposition of carbonate precursors possessed similar morphologies and slightly smaller particle size. The plate-like ceria particles possessed excellent UV-shielding properties, low oxidative catalytic activity, excellent comfort when applied on skin and special metallic sheen color, indicating the high potential in the cosmetic applications.

CB-1:L12 Co-doping Effect of Metal Ion on the visible Light Responsive Photocatalytic Properties of Nitrogen-doped Titanium Dioxide

Peilin Zhang*, Shu Yin, Tsugio Sato, IMRAM, Tohoku University, Sendai, Japan

Metal ions such as Fe3+ and Nb5+ were co-doped with nitrogen ion into titanium dioxide to enhance the visible light responsive photocatalytic activity. Hydrothermal method was employed to prepare the samples using metal chlorides and hexamethylenetetramine as the sources of metal ions and nitrogen ion, respectively. The obtained samples were characterized by XRD, CHN and EDX analysis, BET measurement, and UV-vis reflectance spectra. The co-doping of low-content metal ion didn't have an influence on the crystalline phases and specific surface area (S.S.A.) of the samples. Doping with Fe ion could significantly enhance the absorption in visible light region, but doping with Nb ion showed almost no effect. Decomposition of NO gas under various wavelengths was carried out to evaluate the photocatalytic activities of the smples. The results revealed that co-doping with Nb ion would increase the deNOx ability, but co-doping with Fe ion showed the opposite effect. The difference of co-doping effect was thought due to the different valence of Fe and Nb ions. Co-doping with higher valence metal ion was probably effective in reducing the vacancy in the lattice, which could stabilize the photo-induced electrons and holes, and achieve high photocatalytic activity.

CB-1:L13 Transparent Silica Ambigels through Ternary Azeotropic Mixture

Young-Jei Oh*, Jeon-Kook Lee, Won-Kook Choi, Materials Science and Technology Division, Korea Institute of Science and Technology (KIST), Seoul, South Korea

Great interest in silica nanoporous materials has been attracted. Many investigators tried to find new approaches to crack free and transparent silica aerogels and reduce the complex and long time process of aerogel formation. The wet gel is strengthened by silylation from the aprotic solvents and then dried at ambient pressure. There is no data about a practice of azeotropic mixture in the silica aerogel fabrication process, especially at the ambient pressure drying step. A two-step sol-gel process was performed to prepare monolithic silica ambigels in the temperature range of 130-250 °C. The new method of mesopoure ambigels (aerogels prepared by ambient pressure drying process) synthesis is suggested. This method includes two important points. The first is the SiO2 surface modification of wet gel was performed by 5% TMCS alcohol (n-Butanol) solution. This procedure is provided the silica gel mesopoure structure. The second point is a creation of the ternary azeotropic mixture water/n-Butanol/octane as porous liquid, which is provided the soft two-step gels ambient pressure drying process. The silica aerogels were mesoporous (pore size ~ 50Å), transparent, crack-free with surface area of ~ 1,000 (m2/g), bulk density of ~ 0.4-0.58 (g/cm3) and porosity of 81.9-85%.

CB-1:L14 Use of Additives in the CSD Approach to Oxide Ceramic Layers. The YBCO Example

S. Ricart*, F. Martínez- Julián, X. Palmer, P. Abellan, F. Sandiumenge, A. Pomar, A. Palau, X. Obradors, T. Puig, Instituto Ciencias de Materiales de Barcelona (CSIC), Campus UAB, Bellaterra, Spain

Chemical solution deposition is a very competitive technique to obtain epitaxial films and is considered as one of the promising ways for low-cost production of ceramic materials. The study of different approaches for the formation of epitaxial layers and nanocomposite layers of mixed oxide ceramics, using the MOD-CSD approach, is presented here. As an example of this approach we present some modifications of the TFA-CDS route which is, at present, the most suitable chemical solution road to achieve epitaxial YBCO (HTSC) layers with high critical currents. The use of anhydrous TFA precursors have allowed to shorten the pyrolysis process while understanding the YBCO growth process allows to achieve high critical currents (Jc ≈ 4 MA/cm2 at 77 K). Anhydrous TFA solution proved to be easily modified by changes on concentration, precursors and use of additives. What we present here is different modifications of the standard starting TFA solutions, by using organic, polymeric, inorganic additives and nanoparticles, and their influence on the properties of the resulting YBCO films. With these modified solutions we are able, on one hand, to reduce the fluorine content without loss of the magnetic properties and, on the other hand, to obtain layers with very low porosity, improved planarity and similar high critical currents with reduced growth temperatures. The previously described in situ approach, using a mixture of different salts in the precursor solution, is compared with the new ex situ where a colloidal solution of nanoparticles is used as a solvent for the preparation of the starting precursor solution of Ytrium, Barium and Copper salts in the TFA approach to YBCO nanocomposite layers. The structure and microstructure of the films were investigated by SEM and X-ray diffraction measurements. Critical current measurements, were carried out by a SQUID magnetometer and PPMS.

Acknowledgements - The financial support from MEC (CONSOLIDER NANOSELECT, NAN2004-09133-C03-01, MAT2006-26543-E, MAT2008.01022/NAN); FPU, FPI and RyC), Generalitat de Catalunya (Pla de Recerca SGR-0029 and CeRMAE), and EU (HIPERCHEM, SUPER3C, NESPA)

CB-1:L15 High-performance Si-based Photoceramics via Aqueous Solution Processes Using New Water-soluble Si-compounds

M. Kakihana, Y. Suzuki, S. Tezuka, IMRAM, Tohoku University, Sendai, Japan; V. Petrykin*, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech

We developed a new water soluble silicon compound (WSS), which can be prepared by the reaction between tetraethoxysilane and propylene glycol. WSS can be mixed with neutral water at any ratio, and a stable aqueous solution of WSS with concentration of Si over 2M could be prepared without formation of any precipitation. WSS was extensively used for synthesis of high performance fluorescent materials such as (Y0.79Ce0.01Gd0.20)2SiO5, Zn2SiO4:Mn2+, Ca3Sc2Si3O12:Ce3+ or Ba2SiS4:Eu2+ by aqueous solution-based technologies, which include the so-called hydrothermal gelation (HTG) method, spray drying or freeze drying methods. The HTG is a method based upon hydrolysis of WSS triggered by a hydrothermal treatment leading to formation of gel networks composed mainly of siloxane bonds, in which cations other than Si can be homogeneously dispersed. Preparation of phosphor materials with much higher homogeneity than achievable by the conventional processing resulted in the considerable improvement of fluorescent brightness. The new generation of the stable and water soluble Si compound opens multiple possibilities for the environmentally benign synthesis of Si-based nanophotoceramic materials and development of new materials with superior functional properties using pure water as a solvent.

CB-1:L16 Tailored Silica Based Aerogels for Insulation in Space Environments

L. Duraes*, M. Ochoa, A. Portugal, Department of Chemical Engineering, Univ. Coimbra, Coimbra, Portugal; A. Manaia, J.P. Dias, LED&MAT, IPN-Instituto Pedro Nunes, Coimbra, Portugal; J. Hernandez, R. Patrício, AST-Active Space Technologies, IPN, Coimbra, Portugal

In this work, the sol-gel technology is used to produce silica based aerogels suitable for insulation applications in Space. The properties of the obtained materials are tailored varying the precursor - Methyltrimethoxysilane (MTMS) and Methyltriethoxysilane (MTES), the solvent - methanol or ethanol, and the synthesis conditions. A two-step acid-base catalyzed synthesis is used, which facilitate the separate control of the hydrolysis and the condensation reactions by the variation of the chemicals concentrations and the temperature. Density and thermal conductivity are the critical properties for the sought application. Both are to be made as low as possible. Thus, only highly porous materials can fulfill this requirement. For the synthesis of the aerogels, the drying stage is accomplished by using the supercritical fluid drying technique, to avoid, as far as possible, contraction of the three-dimensional structure of the gel formed in the synthesis stage. The obtained aerogels, either with MTMS or ETMS, show very promising properties for thermal insulation, namely very low density (40-100 kg/m3), very high surface area (~ 400 m2/g) and small pore size (~ 30 Å). They also exhibit moderate flexibility and mechanical resistance, and a remarkable hydrophobic character (> 130°).

CB-1:L17 Microwave Assisted Solvothermal Synthesis and Visible Light Photocatalytic Properties of Nb and N Co-doped SrTiO3 Nanoparticles

U. Sulaeman*, S. Yin, T. Sato, IMRAM Tohoku University, Sendai, Japan

Strontium titanate has been known to possess excellent photocatalytic activity being similar to titania, however it is only active under ultraviolet light irradiation due to the wide-band gap of 3.2 eV. Therefore, to extend the absorption range of strontium titanate into the visible light region, Nb and N co-doped SrTiO3 was synthesized by microwave-assisted solvothermal reaction using SrCl2.6H2O, Ti(OC3H7)4, NbCl5 and HMT (hexamethylenetetramine) in KOH aqueous solution. The products were characterized by XRD, TEM, DRS and BET surface area. The photocatalytic activity was determined by DeNOx ability using LED lamps at 627 nm (red), 530 nm (green), 445 nm (blue) and 390 nm (UV). The nanoparticles of perovskite type SrTi1-xNbxO3-yNy (x= 0-0.2) were successfully synthesized. The photocatalytic activity of SrTiO3 for DeNOx ability in visible light region could be improved by co-doping of Nb5+ and N3-. The excellent visible light photocatalytic activity of this substance may be due to the generation of a new band gap that enables to absorb visible light and decrease in the lattice defects which acts as a recombination center of photoinduced electrons and holes.

CB-1:L18 Soft Solution Processing of Ceramic Powders and Films: Preparation, Properties and Application

Yanfeng Gao*, Hongjie Luo, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China

Crystalline ceramic powders and films with a precise control of polymorphs, crystalline orientations, sizes and morphologies are of technical importance to achieve a wide range of functions. In addition, surface modification of nanoparticles is required to tailor their surface chemistry, so that they can have requisite properties, such as anticorrosion, antioxidization, antireduction, dispersivity, solubility and colloidal stability. Soft solution processes are promising to address the above issues. In this talk, we will present our recent efforts in the study of crystallization engineering, structural design and surface modification of several ceramic oxide systems. The talk involves the solution preparation of TiO2, ZnO, VO2, ZrO2 particles and thin films, and their functional applications.

CB-1:L19 Nano-Boehmite Production and Isocyanite Functionalization of Nano-Boehmite for the Synthesis of Polyurethane Based Coating

G. Eroglu*, U. Colak, B. Mavis, G. Gunduz, Hacettepe Universitesi, Ankara, Turkey; Orta Dogu Teknik Universitesi, Ankara, Turkey

The aim of this study is to produce polymer nano-composites with enhanced physical and mechanical properties to be used in surface coating. Nano-boehmite (NB) particles were produced from aluminum trihydroxide (ATH) by hydrothermal synthesis. The shape and size of NB particles was investigated by scanning electron microscopy (SEM) imaging. 100% of ATH was converted to NB particles and the particle size of NB particles lies between 100-500 nm. Then, NB particles were functionalized with 1,6-di-isocyanatohexane (HDI) and 4,4'-methylene diphenyl diisocyanate (MDI). HDI and MDI were used as a surface grafting agent to react with hydroxyl group on the surface of the NB particles. The reaction between isocyanate groups on the surface of the compound and other carboxyl or hydroxyl terminal groups will result in products with enhanced physical and mechanical properties. The surface properties of the functionalized NB particles were characterized by Fourier Transform Infrared (FTIR) spectroscopy. It was observed that the reaction between isocyanates and hydroxyl groups on the surface of NB was accomplished. In future, functionalized NBs will be used for the production of polyurethane (PU) nano-composites for coating applications and physical and mechanical properties of PU nano-composites will be tested.

Session CB-2
Near-Net-Shape Techniques

CB-2:IL02 Ceramic Injection Moulding for Microtechnology

J. Hausselt, Karlsruhe Institute of Technology and IMTEK, University Freiburg, Germany

Micro ceramic injection moulding (µCIM) is a powerful tool for the fabrication of ceramic microcomponents. For µCIM, however, special requirements have to be met by the so-called feedstocks, consisting of extremely fine powders, binders, and dispersants as well as by the moulding process and by the thermal postprocessing steps like debinding and sintering. The presentation covers the entire process chain of µCIM with emphasis on the special requirements in micrometer dimensions. The development of ceramic feedstocks and their rheological properties which strongly depend on the loading and the size of the powders are addressed and examples of injection moulded ceramic microparts are presented. First explanations on the special impact of low melting binder components on the outstanding bending strength of micro specimens which exceed strength values reported for macroscopic specimens by more than a factor of 3 will be given. Furthermore, first results on two-component-µCIM for the fabrication of either fixed or movable connections between different ceramics will be introduced. Last not least the achievable precision and tolerances will be discussed together with observations of powder-binder segregation mechanisms which seem to limit the precision of µCIM in such small dimensions.

Session CB-3
Polymer-based Processing

CB-3:IL01 **Quo Vadis Polymer-derived Ceramics? Novel Insights in Basic Science and Applications**

Ralf Riedel, Technische Universität Darmstadt, Germany

Preceramic polymers have been proposed over 30 years ago as precursors for the fabrication of mainly Si-based advanced ceramics, generally denoted as polymer-derived ceramics (PDCs). The polymer to ceramic transformation process enabled significant technological breakthroughs in ceramic science and technology, like the development of ceramic fibers, coatings or ceramics stable at ultra-high temperatures (up to 2000 °C) with respect to decomposition, crystallization, phase separation and creep. In recent years, several important advances have been achieved such as the discovery of a variety of functional properties associated with PDCs. Particularly, novel insights into their structure at the nanoscale level has contributed to the fundamental understanding of the various useful and unique features of PDCs related to their high chemical durability or high creep resistance or semiconducting behavior. From the processing point of view, preceramic polymers have been used as reactive binders to produce technical ceramics, they have been manipulated to allow for the formation of ordered pores in the meso-range, they have been tested for joining advanced ceramic components and others. Consequently, possible fields of applications of polymer-derived ceramics have been significantly extended by the recent research & development activities. Several key engineering fields suitable for PDCs will be discussed in this presentation including high temperature resistant materials (energy materials, automotive, aerospace, etc.), hard materials, chemical engineering (catalyst support, food- and biotechnology, etc.), or functional materials in electrical engineering as well as in micro/nano-electronics.

CB-3:IL02 **Processing of SiCO from Polysiloxane-based Preceramic Polymers**

Gian Domenico Soraru, Università di Trento, Dipartimento di Ingegneria dei Materiali, Trento, Italy

Pyrolysis at 1000 °C in inert atmosphere of crosslinked polysiloxanes leads to the formation of amorphous ceramics in the Si-C-O system, the so called silicon oxycarbide glasses. Using a suitable high temperature annealing step the SiCO glasses phase separates and leads to the formation of two interpenetrating C-rich and SiO2-rich networks with typical sizes in the nanometer range. This unique nanostructure leads to unique properties and behaviour: i.e. glass transition temperature above 1350 °C, high temperature visco(an)elastic behaviour and exceptionally high devetrification stability. In this work it will be shown how the composition and the phase assemblage of the Si-C-O materials can be controlled by the appropriate choice of the starting molecular precursors, either via the sol-gel process and from cyclic and linear polysiloxanes crosslinked via hydrosililation reactions. Highlights on the SiCO nanoctructure are presented: the size of the silica clusters is between 1 to 5 nm; XRD and Raman investigations suggest the presence of SiC nanocrystals and graphene layers. Examples of emerging new optical, chemical and electrical properties and possible applications will be given.

CB-3:IL03 **Fabrications of Bulk Si-Based Ceramics and Nanofiber Composites from Polymer Pyrolysis**

Ya-Li Li*, Hua Fan, Xiang Liu, Tian Liang, He-Bao Du, Feng Hou, Key Laboratory of Advanced Ceramic and Machining Technology, Ministry of Education of China, School of Materials Science and Engineering, Tianjin University, Nankai District, Tianjin, P.R. China

The talk will summarize our recent work on the development of bulk polymer-derived ceramics (PDCs), including silicon carbide and silicon oxycarbide, and their composites with carbon nanotube (CNT) fibers. Shaped bulk silicon carbide ceramics are fabricated from polycarbosilanes by thermal crosslinking, warm-pressing and pyrolysis. The ceramic exhibits noticeable mechanical properties such as a high hardness, despite of the presence of oxides in the ceramics introduced from the thermal oxidation of PCS. Net-shaped SiOC bulk ceramics, with tunable compositions and good bonding quality, are fabricated from crosslinkable polysilxoanes through shaping and pyrolysis at various temperatures. The CNT and PDC composites are fabricated by the direct growth of CNTs inside PDCs during its formation. This has been realized by pre-mixing a metal catalyst into a polysiloxane precursor and growing CNTs inside the ceramics under controlled pyrolysis conditions, as demonstrated by the uniform growth of CNTs in the ceramics with good interface bonding with the PDC matrix. This direct growth process is promising to be applied for one-step fabrication of CNT-PDC composites with promising mechanical and electrical properties.

CB-3:IL04 **Electronic Behavior of Polymer-derived Ceramics**

Linan An, Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, FL, USA

Polymer-derived ceramics (PDCs) are a new class of multifunctional high-temperature materials synthesized by thermal decomposition of polymeric precursors. The direct chemical-to-ceramic route of PDCs makes the materials are suitable for varied engineering applications. For example, PDCs are proposed to fabricate high-temperature MEMS and micro-sensors. For such applications, fundamental understanding of the electronic properties of PDCs is required. However, such understanding is not easy to obtain mainly due to the complex structures of PDCs. In this presentation, we investigate the electronic behavior of polymer-derived silicon carbonitride (SiCN) ceramics by characterizing their piezoresistivity, temperature-dependent conductivity and optical absorption. Our results suggest that the conduction of PDCs strongly depends on the concentration of free carbon. With increasing the free carbon concentration, the conduction mechanisms of PDCs transferred from semiconducting to tunneling-percolation. When the materials exhibit amorphous semiconducting behavior, the conduction is strongly affected by the atomic structures and dangling bands. We will correlate results to the structures to reveal the fundamental issues involved in electronic behavior of polymer-derived ceramics.

CB-3:L05 **Nanostructured Boron- and Silicon-based Mesoporous Materials via Preceramic Polymer Nanocasting**

X.-B. Yan, P. Dibandjo, O. Majoulet, J. Alauzun, S. Bernard, P. Miele*, Université Lyon 1, Villeurbanne Cedex, France

Critical technological challenges in various domains such as energy require the development of new ceramic materials with tailored morphologies and enhanced properties. The Polymer Derived Ceramics (PDCs) method is particularly attractive for the formation of nanostructured non-oxide materials in complex forms which cannot be produced by traditional powder processes. The shaping of organized and mesostructured non oxide ceramics is still a challenge since these materials present can be regarded as promising effective catalyst support or molecules adsorbent in devices that have to withstand harsh oxidative and thermal environments. In this contribution, we will describe the synthesis and the characterization of new porous nanostructured boron nitride prepared either by a direct self-assembly method or by a templating process from BN molecular precursors. Mesoporous boron nitride with high specific area (800 m2/g), an important mesoporous volume (0,6 cm3/g), and a narrow distribution of porous diameters (~ 4 nm diameter) has been obtained from templating of carbon CMK-3. We also report the original synthesis of ordered 2-D hexagonal mesoporous SiBCN material using the combination between a nanocasting pathwa and the PDCs approach with a preceramic polymer [B(C2H4SiCH3NCH3)3].

CB-3:L06 **Shaping of Ceramic Fibers and Gradient Porosity Ceramic Bulk Materials Applying UV Curable Dispersions**

Thomas Graule*, Judit Heinecke, Gregor Mueller, Yoram de Hazan, Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for High Performance Ceramics, Dübendorf, Switzerland

In this work we present novel shaping technologies of radiation curable ceramic colloidal dispersions to produce polymer/ceramic and ceramic fibers, microspheres and cellular articles. High loading, low viscosity ceramic nanoparticle dispersions in UV curable monomer mixtures are achieved by a proper choice of monomers or use of special comb-polyelectrolyte surfactants. Novel ceramic/polymer nanocomposite fibers are produced by continuous “on the fly” curing of UV curable colloidal ceramic dispersions structured through a micro-extrusion die. The method is advantageous to obtain multifunctional composite fibers, small diameter ceramic fibers and robo-casting applications. The wide choice of monomers enables composites with tailored properties required for woven products and the low temperature processing benefits biological applications. Selective curing of the flow by narrow beams further distinguishes the technology from conventional ones. UV curable colloidal dispersions containing pore formers are found advantageous for the production of inorganic microspheres and cellular articles. Cellular ceramic articles with controlled cell size and porosity are produced. The use of layer by layer rapid prototyping techniques enables the production of homogeneous as well as gradient porosity monolithic materials with high structural integrity.

CB-3:L08 Synthesis and Characterization of Polycarbosilanes as SiC-based Ceramic Precursors: Applications to Hybrid Material for the Preparation of ZrC-SiC Composites

D. Pizon*, R. Lucas, S. Foucaud, A. Maître, Laboratoire Science des Procédés Céramiques et de Traitements de Surface, UMR CNRS 6638, Université de Limoges, Limoges Cedex, France

Zirconium and silicon carbides are high refractory ceramics with good mechanical properties. In ZrC-SiCp composites, the combination of passivating character of silicon carbide and extremely high melting temperature, hardness, and thermal stability of zirconium carbide, should generate high-performance ceramics. Such properties require a homogenous microstructure in terms of chemical composition and grain size distribution for these materials. The Precursor Derived Ceramics method may be an alternative to reach this purpose. In this way we have undertaken this approach for the preparation of these composites, the key route of this strategy being the use of SiC polymeric precursor synthesised from vinyl silane monomers. The elementary mechanisms of the polymerization and thermal/chemical reticulation of macromolecules so-obtained have been approached. More particular, the role of the molecules/ZrC interactions on the polymerization kinetics and finally on the thermal behaviour of the hybrid materials leading to the ZrC-SiCp composites has been elucidated during the present study.

Session CB-4

Spark Plasma Synthesis and Processing

CB-4:IL01 Modelling of Spark Plasma Sintering Process

E. Olevsky, Dept. of Mechanical Engineering, San Diego University, San Diego, CA, USA

Spark-plasma sintering (SPS) carries a potential for the efficient consolidation of powder materials. The difference in outcomes of SPS and conventional powder hot consolidation techniques can be attributed to the two groups of physical phenomena: of thermal and of non-thermal nature. The first group may include high heating rates, high local temperature gradients, highly non-uniform local temperature distributions, highly non-uniform macroscopic temperature distributions. The second group may include electromigration and intensified diffusion in ionic conductors; electroplasticity mechanisms; ponderomotive forces; electromagnetic “pinch” effect; dielectric breakdown of oxide films and defect generation at grain boundaries. The discussion emphasizing major thermal and non-thermal phenomena contributing to the material transport in field-assisted sintering is presented. Models for spark-plasma sintering taking into consideration selected factors influencing SPS are considered: electromigration, high heating rates, and temperature gradient-driven thermal diffusion. The modeling results agree well with the experimental data on SPS of a metal (aluminum) and ceramic (alumina) powders in terms of SPS shrinkage kinetics.

CB-4:IL02 Shaping of Nanostructured Materials or Coatings Through Spark Plasma Sintering

C. Estournès[1]*, D. Oquab[2], M. Boidot[2], D. Monceau[2], D. Grossin[2], C. Drouet[2], U-Chan Chung[3], F. Roulland[1, 3], C. Elissalde[3], M. Maglione[3], R. Chaim[4], Ph. Miele[5], J. Gurt-Santanach[6], A. Weibel[6], A. Peigney[6], Ch. Laurent[6], [1]CNRS, Institut Carnot Cirimat, Toulouse Cedex, France; [2]Université de Toulouse, UMR CNRS-UPS-INP 5085, CIRIMAT, INPT-ENSIACET, Toulouse cedex, France; [3]ICMCB-CNRS, Université Bordeaux, Pessac Cedex, France; [4]Dept. of Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel; [5]LMI, UMR CNRS 5615, Université Claude Bernard-Lyon 1, Villeurbanne Cedex, France; [6]Université de Toulouse, UMR CNRS-UPS-INP 5085, CIRIMAT, Université Paul-Sabatier, Toulouse cedex, France

Spark Plasma Sintering (SPS) is known to be very efficient for superfast full densification of ceramic nanopowders. This capacity is attributed to the simultaneous application of high density pulsed dc currents and load, even though the sintering mechanisms involved remain unclear. In the first part of the talk, the mechanisms involved during the SPS sintering of two insulating oxide nanopowders (Al2O3 and Y2O3) will be discussed. In the second part of the talk we will illustrate how SPS can also be a useful tool to: (1) Consolidate mesoporous or unstable nanomaterials like SBA-15 or biomimetic apatite, respectively. (2) Densify core (BT or BST)/shell (SiO2 or Al2O3) nanoparticles with limited or controlled reaction at the interface. (3) In-situ prepare surface-tailored Fe-FeAl2O4-Al2O3 nanocomposites, and finally (4) Fabricate in one-step multilayer materials like a complete thermal barrier system on single crystal Ni-based superalloy.

CB-4:IL03 Synthesis of Fine-grained Transparent Oxide Ceramics by Spark-plasma Sintering under Low Heating Rate Control

Byung-Nam Kim, National Institute for Materials Science, Tsukuba, Japan

Fully densified transparent Al2O3 and MgAl2O4 spinel polycrystals were fabricated by spark-plasma sintering (SPS) at low temperatures and low heating rates. For Al2O3 sintered at 1150 °C, the density and light transmission increased with decreasing heating rates. The alumina changed gradually the appearance from opaque to transparent with decreasing heating rates. The grain size decreased from 0.55 µm at 100 °C/min to 0.29 µm at 10 °C/min. The fine microstructure at low heating rates is explained by using the assumption of low defect concentration, and the high density by powder homogenization and enhanced diffusion due to large grain-boundary area. The addition of MgO to the alumina has no noticeable effect on the densification of alumina and resultantly no effect of enhancing the total forward transmission. The MgO doping, however, makes the microstructure less sensitive to the sintering temperature by suppressing grain growth and has an effect of enhancing the in-line transmission. The fine microstructure and high density resulted in a high-strength transparent ceramic. The bending strength of Al2O3 and MgAl2O4 is 850 and 500 MPa, respectively, which are about twice the strength of conventional ones.

CB-4:L04 Densification Mechanism of MgAl2O4 Spinel during Spark-plasma-sintering

K. Morita*, B.-N. Kim, H. Yoshida, K. Hiraga, National Institute for Materials Science, Nano-Ceramics Center, Tsukuba, Ibaraki, Japan

We have recently demonstrated that the density of spinel depends on heating rate during SPS processing: low heating rate is effective for attaining transparent oxide ceramics rather than the widely used high heating rate processing. For a heating rate of 100 °C/min, spinel is low density and almost opaque, whereas for 10 °C/min, transparent spinel can be fabricated for only a 20 min soak at 1300°C. The heating rate dependent porosity can be related to densification mechanisms. The present study was therefore performed to examine the densification mechanisms during SPS processing. As density ρ increases, that is, as effective stress seff decreases, stress exponent n evaluated from seff dependence of densification rate varies from $n > 4$ at low ρ, $n \sim 2$ at intermediate ρ to $n \sim 1$ at high ρ. TEM observation shows that significant stacking faults caused by partial dislocations are observed at the low ρ, but limited at high ρ. The ρ dependent densification behavior and microstructure suggest that the predominant densification mechanism in SPS processing changes with ρ from plastic flow by partial dislocation motion for the low ρ ($n > 4$), dislocation-accommodated grain boundary sliding for the intermediate ρ ($n \sim 2$) and diffusion-related creep for the high ρ ($n \sim 1$).

CB-4:L05 Effect of CeO2 Addition on the Mechanical Properties of Al2O3-ZrO2 Ceramics Prepared by Spark Plasma Sintering

E. Yilmaz, O. Ormanci, I. Akin, F. Sahin, O. Yucel, G. Goller*, Istanbul Technical University, Metallurgical and Matls Eng. Dept, Istanbul, Turkey

Alumina and zirconia ceramics are widely used for orthopedic implants due to their excellent mechanical properties, high wear resistance and biocompatibility. It is known that Al2O3 -Y-TZP-CeO2 composites have a good balance between toughness and strength. In this study, monolithic Al2O3 and Al2O3/3Y-TZP (90-10 vol%) and Al2O3/3Y-TZP with 5 wt% CeO2 composites were prepared by spark plasma sintering (SPS) at temperatures of 1350, 1460 °C and 1450 °C for 300 s under a pressure of 40 MPa, respectively. Shrinkage of the specimens during

SPS process was continuously monitored. Densities of the composites were determined by the Archimedes' method. Vickers hardness (HV) was measured under loads of 9.8 N. Fully dense Al_2O_3 and Al_2O_3/3Y-TZP composites containing 0 and 5wt% CeO_2 with a relative density of 97% were obtained. Vickers hardness of the composites decreased with increasing CeO_2 content from 19.8 ± 0.4 GPa to 17.0 ± 0.3 GPa. Bending strength of Al_2O_3/3Y-TZP with 5 wt % CeO_2 densified by SPS at 1450 °C reached 374.6 MPa under loads of 1579 N.

CB-4:L06 Spark Plasma Sintering of Iodine-bearing Apatite

S. Le Gallet*, F. Bernard, Laboratoire ICB, Université de Bourgogne, Dijon, France; L. Campayo, E. Courtois, F. Bart, CEA, DEN, Marcoule, DTCD/SECM/LDMC, Bagnols-sur-Ceze, France; S. Hoffmann, Yu. Grin, Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

The high chemical durability of iodine-bearing apatite makes it strongly prospective for conditioning of radioactive iodine. The synthesis and consolidation of iodine-bearing compounds require low temperatures to avoid iodine volatilization. Spark plasma sintering therefore appears to be a suitable process because of its shorter treatment time and lower sintering temperature compared with other processes such as HUP or HIP. Two alternatives were examined: SPS sintering of iodine-bearing apatite powder and SPS reacting of a stoichiometric lead iodide and lead phosphovanadate powder mixture. The degree of densification and the microstructure of bulk materials in both cases are described and compared. Reactive sintering appears to involve a three-stage mechanism: (i) PbI_2 coalescence, (ii) solid-state iodoapatite synthesis and consolidation and, (iii) iodoapatite consolidation in the presence of a liquid phase. The SPS reacted products reveal the finest and most homogeneous microstructure, and a density exceeding 96%.

CB-4:L08 Effects of the SPS Parameters on the Reactive Sintering of a Cobalt Aluminate Powder

A. Pavia*, C. Estournes, A. Weibel, A. Peigney, G. Chevallier, Ch. Laurent, Université de Toulouse, CIRIMAT, UMR CNRS-UPS-INP 5085, Université Paul-Sabatier, Bât. 2R1, Toulouse cedex, France; C. Estournes, G. Chevallier, PNF2 CNRS, MHT, Université Paul-Sabatier, Toulouse cedex, France

Spark Plasma Sintering (SPS) allows one to obtain highly densified materials with better control of their microstructure at lower temperatures and shorter dwell times than conventional sintering technique like Hot Pressing (HP). The participation or effect of electric current during the SPS sintering remains a major research focus. A cobalt aluminate powder (a blue pigment, called Thénard's blue) was synthesized by combustion and sintered by SPS. The influence of different parameters (temperature, pressure, heating rate, pulses sequences) is studied. During the SPS treatment, $CoAl_2O_4$ is reduced, from 1200 °C onwards, at the surface of the material, i.e. on the faces in contact with the plungers. This results in the formation of a Co-Al_2O_3 composite layer, the thickness of which (50-400 µm) varies depending on the SPS parameters. The results on the microstructure of the materials will be discussed.

CB-4:L09 Spark Plasma Sintering of AlON Ceramics

H.E. Kanbur*, F.C. Sahin, O. Yucel, G. Goller, Istanbul Technical University, Istanbul, Turkey

Aluminum oxynitride ceramics (ALON) were prepared by Spark Plasma Sintering (SPS). AlN and Al_2O_3 mixtures with 35.7 mol% AlN were prepared with ball milling for 24 h. The powder mixtures were sintered at several temperatures and periods at 40 MPa in nitrogen atmosphere by SPS system. The compositions of the system were examined by X-ray diffraction (XRD). The hardness, fracture toughness and microstructure of the sintered samples were investigated and discussed in detail.

CB-4:L10 Spark Plasma Sintering of a Conductive Material, YZrTiO

L. Ramond*, G. Bernard-Granger, A. Princivalle, C. Guizard, LSFC - UMR 3080 CNRS - Saint-Gobain CREE, Cavaillon, France

We have investigated the spark plasma sintering (SPS) of a mixed conductive powder, YZrTiO. This material was synthesised by a sol-gel route, then annealed at a specific temperature to lead to the crystallization of YZrTiO. An experimental matrix for the SPS was chosen to identify the mechanism of densification. Finally, the conductivity of the dense spark plasma sintered pellets was measured by impedance spectroscopy. These results have been compared to those obtained for pressureless sintered pellets.

CB-4:L11 Production and Characterisation of Boron Carbide - Titanium Diboride Ceramics by the Spark Plasma Sintering Method

Berkay Uygun*, Gultekin Goller, Onuralp Yucel, Filiz Sahin, ITU Departent of Metallurgical and Materials Engineering, Istanbul, Turkey

This study was carried out to produce and characterise B_4C - TiB_2 ceramics by spark plasma sintering for the improvement of low sinterability and low strength of B_4C. TiB_2 powder was added in order to improve the strength of flexibility and fracture toughness of the B_4C ceramic compounds. B_4C and TiB_2 powders (3.03 and 5.86 microns respectively) were initially mixed in ethanol solution with ZrO_2 beads using a 400 rpm-mixer for 1 hour. In the sintering step, 5, 10, 15 and 20 volume % TiB_2 containing mixtures were used and sintered by SPS method in disc-shaped graphite dies. The obtained products were characterized by using X-ray diffraction and SEM techniques. The hardness values were measured under 1000 g load and the density values were measured with Archimedes' principle. The 3-point bending tests were also conducted as well as modulus of elasticity measurements under 500 g load by using indentation method.

Session CB-5

Microwave Processing

CB-5:IL01 Microwave Processing of Ceramic-based Materials: Latest Developments and Trends

Monika Willert-Porada, Chair of Materials Processing, Faculty of Engineering Science, University of Bayreuth, Bayreuth, Germany

The importance of ceramic based materials is increasing constantly because of their broad range of functional properties as powders, coatings, films, membranes, fibres as well as in bulk parts. Traditionally, powder synthesis and sintering is applied for processing of ceramic materials. But also melt processing and deposition from gas phase is gaining importance, particularly for coatings and high surface area ceramic materials. The range of heating and sintering technologies has been widened by application of new energy sources, namely electrical heating with direct and alternating currents of various frequency as well as plasma heating and hybrid heating methods. In addition, the dynamic range of energy deposition has been extended by the need to achieve very high process temperature in a very small volume of material. The lecture presents the latest developments and trend for microwave and microwave assisted processes to synthesize ceramic powders and to process coatings, membranes as well as bulk parts, over a temperature range up to sintering and melting temperature. Besides technology and material aspects the current level of theoretical understanding of microwave heating will be briefly discussed.

CB-5:IL02 Synthesis of High Performance Ceramics Materials via Microwave Processing

Hirotsugu Takizawa, Department of Applied Chemistry, Tohoku University Sendai, Japan

Microwave heating is rapidly becoming an established procedure for inorganic synthesis. The microwave heating technique has stimulated interest in recent years, because of its potential advantages, including a significant reduction in manufacturing costs due to energy savings and shorter processing times. Moreover, it has many advanced features, for example, the development of fine microstructures and improvement in chemical and physical properties. These features are believed to be due to the "non-equilibrium reaction field" of microwaves. The current topics of microwave processing of inorganic materials achieved in our laboratory are presented. In some cases, selective heating of a specific component of reaction system plays a key role on the formation of non-equilibrium structure. Microwave processing is essentially "non-equilibrium reaction" because microwave absorbing behavior strongly depends on a nature of a material. For example, if a specific component in a chemical reaction system strongly couples with microwaves and the other component does not, the diffusion rate at the interface will be much different. In such a case, we expect "one-way diffusion" in a microscopic scale. This situation is a key factor to form a thermally non-equilibrium state.

CB-5:IL03 Microwave-assisted Routes to Inorganic Particles and Films in Organic Solvents

Markus Niederberger, Laboratory for Multifunctional Materials, Department of Materials, ETH Zurich, Zurich, Switzerland

Liquid-phase routes to metal oxide nanoparticles in organic solvents under exclusion of water have become a versatile alternative to aqueous methods. A special feature of these routes is that organic reactions provide the “monomers” for the nucleation of the inorganic nanoparticles, and these organic reactions can be controlled by applying microwave irradiation. Subtle control of the irradiation time, the temperature and the out-put power makes microwave-assisted nonaqueous chemistry a perfect model system for the study of nanoparticle formation. Based on ZnO as an example we will discuss, how nanoparticle formation and growth can be described by combining kinetic analysis of the precursor consumption with the crystal growth. These results are of high practical relevance, because they allow a precise tuning of the crystal size and a highly efficient doping of the metal oxides with transition metals. Furthermore, we will present how the microwave-assisted liquid-phase synthesis can be extended to the preparation of metal oxide films and to other classes of functional materials such as lithium metal phosphates for battery applications.

CB-5:L04 **Microwave Absorbency Change of Zirconia Powder and Fiber during Vacuum Heating**

S. Sano*, S. Kawakami, Y. Takao, S. Takayama, Y. Sato, AIST, Nagoya-city, Aichi, Japan; NIFS, Toki-city, Gifu, Japan

Stabilized zirconia shows rather high microwave absorbency, and the absorbency become higher at high temperature. In this study, stabilized zieconia powder, partially stabilized zirconia powder and zirconia fiber were subjected for microwave absorption measurements at elevated temperature. Microwave absorption measurements were done by using a system consisting of a microwave vector network analyzer, a circular wave-guide fixture and a vacuum furnace. Microwave absorbency was evaluated by the reflection power change from sample under vacuum heating. Microwave absorbency of stabilized zirconia gradually increased with the increase of temperature. We supposed that the increase of microwave absorbency is related to the ionic (oxygen) conduction behavior of stabilized zirconia. Stoichiometric composition ZrO2 powder was also subjected for a measurement to consider the relation between microwave absorbency and ion conduction of zirconia.

CB-5:L05 **Microwave Assisted Reaction Sintering of ZrSiO4/α-Al2O3 Mixture**

O. Ertugrul*, S. Akpinar, I.M. Kusoglu, K. Onel, Dept. of Metallurgical and Materials Engineering, Dokuz Eylul University, Buca-Izmir, Turkey

In-situ formation of ZrO$_2$-mullite composites will result in better mechanical properties than mullite ceramics. Zirconia-mullite composition can be obtained by reaction sintering of ZrSiO$_4$ and α-Al$_2$O$_3$**.** The samples were prepared from high-purity (99.9%) alumina and fine zircon(ZrO$_2$>65 wt.%) powders using PVA as binder. The mixed powders were dry-pressed and then sintered in a multimode microwave field of 2.45 GHz. The microwave effect on ZrSiO$_4$ dissociation and mullite formation was evaluated by comparing the microwave and conventional sintered samples. The as-reacted powders were characterized by X-ray diffraction and scanning electron microscopy(SEM) to confirm the phase formation. Effect of various sintering parameters on mullitization and mullite grain growth were investigated.

Session CB-6
Bio-inspired and Bio-enabled Processing

CB-6:IL01 **Formation of Hierarchically Structured Crystals through Bio-inspired Processing**

H. Imai*, Y. Oaki, Faculty of Science and Technology, Keio University, Yokohama, Japan

A multilevel hierarchy of lengths from nanometer to millimeter is commonly observed in the sophisticated architectures of various biominerals. Especially, the superstructures of carbonate-based biominerals were categorized as mesocrystals, which are broadly comprised of crystallographically oriented crystals. Here, bio-inspired processing by using self-organized crystal growth in aqueous solution systems is proposed for the production of hierarchical mesocrystals composed of various inorganic materials. Bridged-type mesocrystals consisting of regularly assembled inorganic segments were obtained through crystal growth directed with adsorption of specific soluble agents and/or with a diffusion filed in gel matrix. Arranged architectures of nanometric units were induced with the capping effect of the molecules adsorbed on the surface of inorganic crystals. Micrometric oriented structures were formed with the matrix effect which controlled the diffusion of solutes and the driving force of crystallization. Multilevel superstructures similar to the biological architectures were precisely achieved by a combination of the capping and matrix effects with soluble and insoluble agents.

CB-6:IL02 **Integration of Bio-Enabled and Synthetic Syntheses of Functional 3-D Nanostructured Assemblies**

K.H. Sandhage[1,2]*, S.C. Davis[1], J.P. Vernon[1], A.S. Gordon[1], J.D. Berrigan[1], S. Shian[1,2], Y. Fang[1], Y. Cai[1], M.B. Dickerson[1,3], R.R. Naik[3], S.R. Marder[2,1], N. Kroger[2,1], [1]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA; [2]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA, USA; [3]Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson Air Force Base, OH, USA

The precise, reproducible, and scalable fabrication of three-dimensional nanostructures with a wide variety of complex shapes and tailorable chemistries remains a difficult challenge. Nature provides awe-inspiring examples of organisms capable of synthesizing intricate 3-D inorganic and organic nanostructured assemblies (e.g., diatoms, brittlestars, butterflies). However, while bio-derived nanostructures with a wide variety of shapes can be found in nature, the range of bio-inorganic (bioclastic) chemistries is quite limited. The chemistries and properties of bio-derived 3-D assemblies can be appreciably expanded via the BASIC (Biological Assembly and Shape-preserving Inorganic Conversion) process. In this presentation, several reaction-based and coating-based BASIC approaches for converting inorganic and organic 3-D biotemplates into replicas comprised of a variety of other functional chemistries (e.g., oxide, metal, polymer, composite) will be described. Adaptation of these shape-preserving chemical conversion processes to synthetic structures will also be discussed.

”Shaped Microcomponents via Reactive Conversion of Biologically-derived Microtemplates,” U.S. Patent 7,067,104; “Shaped Micro-components via Reactive Conversion of Synthetic Microtemplates,” U.S. Patent 7,393,517.

CB-6:IL03 **Bio-inspired Synthesis of Oxide-based Ceramics**

J. Bill, Institute for Materials Science, University of Stuttgart, Stuttgart, Germany

At present, large research efforts are carried out with regard to the preparation of ceramics without sintering and expensive equipment. Living nature provides paradigms for new synthesis pathways, which occur at ambient conditions and by apparently simple means. In this connection, biomineralization yields highly complex organic/inorganic structures, e. g. within nacre. In general, the formation of such biominerals involves organic molecules that act as templates during the mineralization of the inorganic phases. The aim of bio-inspired processing routes is the imitation of such principles by technical means. Within this contribution the bio-inspired deposition of ceramics like zinc oxide and titania from suitable metal salt solutions is demonstrated. (Bio)organic molecules like polyelectrolytes, amino acids, peptides, proteins, DNA as well as self-assembled monolayers are applied to trigger the nanostructure evolution of the ceramics. Examples for the architectural design of oxide-based ceramics based on the structural features of biominerals will be given. In addition, the mechanical and the functional properties of the obtained materials are discussed.

CB-6:IL04 **Nano-structured Ceramic Films by Aerosol Deposition**

Dong-Soo Park*, Byung-Dong Hahn, Woon-Ha Yoon, Jungho Ryu, Jong-Jin Choi, Byoung-Kook Lee, Junhwan Choi, Functional Materials Division, Korea Institute of Materials Science, Changwon, Gyeongnam, South Korea

Aerosol deposition is a kind of coating methods to make dense ceramic films by spraying ceramic powders in vacuum at room temperature. Nano-structured ceramic films free from any observable pore or crack can be made from the powders with much larger particle size. A variety of applications of Aerosol deposition are possible. In this presentation, we would like to introduce our activity on bioactive calcium phosphate based composite films including hydroxyapatite (HA), Si-HA, HA-CNT and others. The films on titanium metal substrate exhibited strong tensile adhesion strenth (>25 MPa), excellent bio-compatibility in both in-vitro and in-vivo tests. Also, we would like to briefly introduce other possible applications.

CB-6:L05 **Effect of the Hydrothermal Heat Treatment Conditions of Titanium on the Coating of Bio-mimetically Grown “Bone-Like” Apatite Layer**

D. Teker*, C. Poyraz Sag, M. Dinçer, S. Alkoy, K. Öztürk, Gebze Institute of Technology, Material Science and Engineering, Kocaeli, Turkey

Titanium surfaces were modified hydrothermally for bio-mimetic coating process using 1.5X simulated body fluid (SBF). Two different aqueous environments were used for ion implantation on the titanium in the hydrothermal modifications: only de-ionized water and CaO-de-ionized water. CaO was used as calcium source and 0.02 mol of it per liter of de-ionized water was selected as the fixed concentration. Two different hydrothermal conditions were used as: at 200 °C under 1.5MPa pressure, and at 230 °C under 2.5MPa pressure. The outer-most surface layers became rich with Ca when Ca- containing hydrothermal environment was used. This result was verified using XPS. The surface-modified specimens were immersed in SBF to be coated with active “bone-like” apatite mineral by bio-mimetic process. They were immersed for four different periods: 1, 2, 3 and 4 weeks. The apatite accumulations on specimens were determined as a function of soaking time. SEM, XRD and FTIR were evaluated on coatings. The results indicated that the hydrothermal heat treatment conditions affect the quality of the coating layer. The titanium surfaces hydrothermally treated at 230 °C and under 2.5MPa were completely covered in a shorter period of time than the surfaces treated under milder hydrothermal conditions.

Session CB-7
Hybrid Materials

CB-7:IL01 **Novel Strategies for the Design of Nanostructured Advanced PorousMaterials**

C. Sanchez, Laboratoire de Chimie de la Matière Condensée de Paris, CNRS, Université Pierre et Marie Curie, Collège de France, Paris, France

Hybrid inorganic-organic materials can be broadly defined as synthetic materials with organic and inorganic components which are intimately mixed. They can be either homogeneous systems derived from monomers and miscible organic and inorganic components, or heterogeneous and phase-separated systems where at least one of the components’ domains has a dimension ranging from a few Å to several nanometers. Research on hybrid molecular or nanocomposites has experienced an explosive growth since the 1980s, with the expansion of soft inorganic chemistry processes. The mild synthetic conditions provided by the sol-gel process such as metallo-organic precursors, low processing temperatures and the versatility of the colloidal state allow for the mixing of the organic and inorganic components at the nanometer scale in virtually any ratio. These features, and the advancement of organometallic chemistry and polymer and sol-gel processing, make possible a high degree of control over both composition and structure (including nanostructure) of these materials, which present tunable structure-property relationships. This, in turn, makes it possible to tailor and fine-tune properties (mechanical, optical, electronic, thermal, chemical…) in very broad ranges, and to design specific systems for applications. Hybrid materials can be processed as gels, monoliths, thin films, fibers, particles or powders. The seemingly unlimited variety, unique structure-property control, and the compositional and shaping flexibility give these materials a high potential. Indeed, hybrid materials are already commercial. A distinct characteristic of hybrid materials is that their properties are related not only to the chemical nature of the inorganic and organic components but they rely heavily on their synergy. Therefore, the interface between inorganic and organic domains is of paramount importance. Indeed, one key point is the control of this interface, the *hybrid interface*. The general chemical pathways used to obtain hybrid materials include: from mutual dispersions of polymer domains attainable by the relatively simple combination of sol-gel techniques and polymerization, to the assembly of well defined nanobuilding blocks (NBB), by using separators, or polymerisation of functional NBB, to organised pore systems, obtained by the combination of sol-gel and self-assembly techniques. Materials with hierarchical structures and complex forms can be also obtained by “integrative pathways”, i.e. by combining controlled phase segregation, selective interactions and morphosynthesis to the sol-gel/self-assembly tandem. Novel phases, composites or dispersions bearing original properties (chemical storage, sensors, controlled delivery,…) can be created, which will have a deep impact in the technology of the 21st Century. The *integrative chemical construction* and patterning of materials with long-range order architectures (beyond nanometer size) remains an important challenge in the new field of “organised matter chemistry”. This conference will present some examples of nanostructured *(obtained via self-assembly)* and hierarchically structured materials inorganic and hybrid organic-inorganic materials.

CB-7:IL02 **Morphosynthesis of Nanoporous Materials by Microwave**

Sang-Eon Park, Lab. of Nano-Green Catalysis and Nano Center for Fine Chemicals Fusion Tech., Dept. of Chemistry, Inha University, Incheon, Korea

Microwave syntheses of both microporous zeolites and mesoporous materials have been obtained through the controlled synthesis of phases, morphologies, functionalization and nanostructuring for catalytic and nanoscopic applications. The microwave technique has been regarded as a novel synthesis tool due to some beneficial advantages such as homogeneous nucleation to give smaller nucleation and uniform crystals having rather larger external surfaces, rapid rates in the synthesis times together with the phase controlled synthesis, facile morphology control, greener synthesis as an energy efficient way and so on. And it allows direct co-condensation during sol-gel synthesis which resulted in morphosynthesized organo-inorganic structures and rather facile incorporation of heteroatoms onto the zeolitic frameworks and more hydrophobicity than those of hydrothermally synthesized materials by depriving hydroxyl groups. Further, microwave syntheses have often proven to create unique pore channel orientation, which gave useful characteristics in the catalysis of organic reactions due to the confinement.

CB-7:IL03 **Co-assembly of Ceramic Nanosheets with Drug Molecules for Nanomedicine**

J.H. Choy, Center for Intelligent Nano-Bio Materials (CINBM), Department of Bioinspired Science (WCU Program), Department of Chemistry and Nano Science, Ewha Womans University, Seoul, Korea

The drug delivery system (DDS) becomes important in the view point of health and welfare of human being in the near future, since it allows target-specificity and cellular penetration efficacy of drug molecules. Most of researches on drug delivery carriers have been restrictively focused on plasmid, polyethylene glycol and etc. According to the cell line experiments, however, the drugs or genes co-assembled with ceramic nanosheets of layered double hydroxides (LDHs) can be more effectively transferred into the cell by clathrin-mediated endocytosis. Since ceramic nanoparticles of LDH are partially soluble in cytosol, the drug concentration in the cell increases and as a consequence, the drug efficacy is maximized. More recently, we attempted to apply the present nano-bio co-assembling technology to the boron neutron capture therapy (BNCT), since it has long been needed to develop a boron carrier to deliver boron-containing molecules into cells sufficiently. The present B-LDHs did not show any cytotoxicity in-vitro and eventually any influence on cell viability upto the concentration of 250 µg/ml. Due to its high neutron capture efficiency, we concluded that the present combined BNCT-DDS could provide a promising integrative therapeutic action in chemo-radiation cancer therapy.

CB-7:IL04 **Mesoporous Silica Nanoparticles for Cell Specific Targeting and Drug Delivery**

Mika Lindén*, Jessica Rosenholm, Department of Physical Chemistry, Abo Akademi University, Turku, Finland; Cecilia Sahlgren, Department of Biology, Abo AKademi University, Turku, Finland

One of the big challenges of medicine today is to deliver drugs specifically to the defected cells. This is of special importance in cancer treatment, as many of the pharmacological agents developed are harmful for non-cancerous cells. Intersecting chemistry, materials science, pharmaceutical technology and biology, results will be presented related to the use of multifunctional mesoporous silica nanoparticles as drug delivery systems to specifically target cancer cells, in combination with concurrent real-time in vitro or in vivo monitoring (imaging). Due to the large surface area and the controllable surface functionality of the particles they can be loaded with large amounts of drugs and coupled to molecules of choice for targeting purposes, simultaneously carrying traceable (fluorescent or magnetically active) modalities. Thus, the NP system can be used not only to specifically deliver drugs (therapeutic action) but also for medical imaging (diagnostic action).

CB-7:IL05 **Panascopic Assembling of Ceramic Materials for High Performance UV-ray Shielding Application**

Tsugio Sato*, Xiangwen Liu, Shu Yin, IMRAM, Tohoku University, Sendai, Japan

Semiconductor nanoparticles are used as inorganic UV-shielding materials, however, the comfort of inorganic nanoparticles are generally modest due to the agglomeration of nanoparticles. The hybrid materials consisting of plate-like potassium lithium titanate (K0.8Li0.27Ti1.73O4) micro particles coated with calcia-doped ceria (Ce1-xCaxO2-x) nano particles were prepared by the co-precipitation method and sol-gel method. Co-precipitation method: after dispersing K0.8Li0.27Ti1.73O4 particles in deionized water at 40 °C, appropriate quantities of 3 M NaOH aqueous solution and 0.8 M CeCl3-0.2 M CaCl2 mixed aqueous solution were simultaneously dropped, followed by adding desired amount of H2O2 solution to precipitate Ce1-xCaxO2-x. Sol-gel process: after adding CH3COOH in Ce(NO3)3.6H2O-Ca(NO3)2.4H2O mixed ethanol solution at 40°C with an CH3COOH/(Ce+Ca) molar ratio of 10, desired amounts of K0.8Li0.27Ti1.73O4 particles dispersed in ethanol were dropwise added. Then, the solution was heated at 60 °C for 2 h to get gel-like substance, followed by drying in a vacuum oven at 60 °C for 5 h and calcination at 800 °C for 2 h. The comfort when applied on skin and UV-shielding ability of the sample prepared by the sol-gel method were superior to those by the co-precipitation method.

CB-7:IL06 Energy Generation and Storage Applications of TiO_2 Nanotubular Arrays by Atomic Layer Deposition and Nanotemplating

Hyunjung Shin, School of Advanced Materials Engineering, Kookmin University, Seoul, Korea

Tubular structures of oxides in nanometer length scale have attracted much attention as one of the most promising one-dimensional (1-D) materials for many applications. Unlike nanowires, the inner surfaces can add more functionalities as well as accessibilities. Several different fabricating methods of nanotubes (NTs) have been proposed and did not show enough crystalline quality of NTs. High crystalline quality of TiO_2 NT arrays templating by atomic layer deposition (ALD) onto anodic aluminum oxides (AAO) and subsequent annealing, will be presented in this talk. By simply changing the wall thickness of NT's, the optimum boosting condition of crystallization has been attained. More than half of micron-meter long anatase single grains in the NTs resembling the physical properties of the original bulk materials in NTs were obtained, and the most defective form was able to be prepared by pinning the grain growth at the thinnest wall thickness (< 5nm in thickness). The former was utilized in the fabrication of high efficient dye-sensitized solar cells, producing reproducible photovoltaic cells exceeding overall photon-to-electricity conversion efficiency of ~6%, and the high efficiency results were ascribed to the minimization of defect sites for electron trapping. The latter was found to be using in Li-ion secondary battery application, resulting in ultra-fast charging capability up to ~2000 C as well as high charging capacity. The achievement is considered to be the presence of rich grain boundary defects which are easily accessible to Li-ions. The present ALD grown TiO_2 NTs should hold a position of new materials system at the interface of 1- to 3-D for function-driven novel applications.

CB-7:L07 Exploring Inorganic-Organic Interfaces in Hybrid Materials with Advanced NMR Tools

N. Folliet, N. Baccile, T. Azais, C. Gervais, G. Laurent, C. Bonhomme, F. Babonneau*, Laboratoire de Chimie de la Matiere Condensee de Paris, Universite Pierre et Marie Curie-UPMC and CNRS, College de France, Paris, France; P.M. Aguiar, D. Sakellariou, Laboratoire de Structure et Dynamique par Resonance Magnétique, Service Interdisciplinaire sur les Systemes Moleculaires et les Materiaux (Laboratoire Claude Frejacques, CNRS URA 331) DSM/IRAMIS/SIS2M, CEA Saclay, Gif-sur-Yvette, France

A large number of combinations between the organic and inorganic components exists in hybrid materials. Very complex structures can thus be obtained with multiple interfaces, for which solid state NMR appears a powerful and versatile characterization method. In this presentation, interactions between silica surface and organic moieties will be investigated. They can be probed using 1H-29Si as well as 1H-1H dipolar couplings; 1H-29Si-1H double cross polarization techniques was used to selectively detect proton sites at the silica surface while 1H Double Quantum (DQ) NMR allowed to localize organic groups at the silica surface. This last experiment was even extended to thin film samples using the Magic Angle Coil Spinning (MACS) approach. This innovative technique is very suitable for very small amount of sample (0.1 mg), and should open extremely interesting opportunities to characterize organic-inorganic thin films. Finally, computer modeling including DFT and VASP methods will be presented in connection with solid state NMR experiments and GIPAW method, which is now a well established tool of calculation for NMR parameters. This combined approach is currently used to get a better description of interface between an hydroxylated amorphous silica surface and organic molecules.

CB-7:L08 Thermal and Dimensional Stability of Filled Hybrid Foam

Ming-Yung Chen[1]*, Chenggang Chen[1, 2], [1]Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson AFB, OH, USA; [2]University of Dayton Research Institute, Dayton, OH, USA

Availability of advanced materials has opened up opportunities in meeting several functional requirements through hybridization. Hybrids consisting of ceramics, metal sand high performance polymers could benefit many aircraft and space satellite applications. They could meet requirements of low weight, high environmental stability, and high thermal or dimensional stability. In this study, hybrid materials consisting of high performance polymer, porous ceramics and other constituents such as glass micro balloons, Zircornium Tungstate (with negative coefficient of thermal expansion (CTE)) and nanoclay were studied. Specimens were successfully produced with a range of density from 0.2 to 1.1 g/cm3depending on the degree of fill in the foams. CTE tailoring was achieved to greatly reduce the residual stress arising from processing and CTE mismatch of dissimilar materials. The evaluations of thermal and dimensional stability were examined from thermal exposure with TGA, DSC, and TMA analysis. The synergistic effects of resin, ceramic constituents and pores on the hybrid properties will be presented.

CB-7:L09 In-situ TEM Observation of the Crystallization Process for Li NbO3 and NaNbO3

H. Nakano, Toyohashi University of Technology, Toyohashi, Japan; Y. Suyama, Shimane University, Japan

Fabrication of advanced electronic components requires high-quality powders. In this work, nano-powders of Li and/or Na niobates are synthesized from (Li and/or Na)-Nb ethoxide by a sol-crystal method. A single crystal of (Li and/or Na)-Nb ethoxide is decomposed to an amorphous matrix below 473 K. Next, small crystals are grown by heating at the appropriate temperature for each specimen. The sol-crystal method provides homogeneous quality and fine grains by heating at lower temperature. Structural analysis of the powders is performed by transmission electron microscopy (TEM) and X-ray diffraction. As a result, LiNbO3 turns to dense-powders, but NaNbO3 forms nano-porous powders. In order to understand this difference, we try to observe in-situ the crystallization and grain growth processes by high-temperature TEM. We successfully observe in-situ this processing and discuss the structural change and formation mechanism of LiNbO3, comparing these features with those of NaNbO3 and (Li, Na)NbO3.

CB-7:L10 Ceramic/Polymeric Hybrids with Reduced Coefficients of Thermal Expansion

Chenggang Chen[1, 2], Kevin H. Hoos[1, 3], Ming Y. Chen[1], [1]Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson AFB, OH, USA; [2]University of Dayton Research Institute, Dayton, OH, USA; [3]Southwestern Ohio Council for Higher Education, USA

The mismatch of the coeffiecient of the thermal expansion (CTE) is one of the main leading causes to crack initiation and delamination of the carbon fiber-reinforced composites and metal/hybrid materials. In this research, a ceramic material (zirconium tungstate) with negative-CTE was incorporated with thermoset polymers (epoxy and polyimide). The morphology obtained from SEM showed good dispersion of the zirconium tungstate particles. Much reduction in CTE was achieved by as much as ~40% by their incorporation. Significant improvement in thermal stability was also achieved. Effects of starting material, particle size, and processing on properties will be presented. Comparisons of the experimental CTE values with the rule-of-mixture and the analytical micromechanical models will be discussed.

CB-7:L11 Dimension- and Direction-controlled Gold Nanorods Deposited in Ordered Mesoporous Silica

G. Kawamura*, I. Hayashi, R.A. Fitrah, J. Hamagami, M. Sakai, A. Matsuda, Toyohashi University of Technology, Toyohashi, Japan; H. Muto, Kurume Natl. Col. Technol, Japan

Gold nanorods (GNRs) possess attractive optical properties, whose origin is localized surface plasmon resonance (LSPR), and that is sensitively dependent on their dimension, and the adjacent state. In this study, ordered mesoporous silica with 2-dimensional hexagonal pores (SBA-15) was used as a template to control the dimension, direction, and the arrangement of GNRs. The GNRs were confined in the tubular pores of SBA-15 so that the diameter of GNRs was fixed at ca. 8 nm (the pore diameter of SBA-15 was ca. 10 nm). The length, direction, and the arrangement of GNRs were controlled by changing the concentration of the used chemicals including gold precursor and the pore structure of SBA-15. The optical properties of the dimension-and direction-controlled GNRs deposited in SBA-15 were measured throughout the ultra violet-visible-near infrared region, and showed a good correlation to the well ordered GNRs arrangement observed using transmission electron microscope.

Session CB-8
Porous Ceramics

CB-8:IL01 Confined Molecules in Porous Media for Controlled Release: NMR Characterization

T. Azais*, N. Folliet, G. Laurent, F. Babonneau, Université Pierre et Marie Curie-Paris6 and CNRS, UMR 7574, Lab. Chimie de la Matiere Condensee de Paris, France; F. Guenneau, A. Nossov, Universite Pierre et Marie Curie and CNRS, Lab. de RMN des Matériaux Nanoporeux, FRE 3230, Paris, France; D. Aiello, F. Testa, Dept. of Chemical Eng. and Matls, CR-INSTM, University of Calabria, Arcavacata di Rende (CS), Italy

Drug molecules confined in porous media are a new class of materials intensively studied in reason of their ability to increase the solubility of hydrophobic drugs in biological fluids. On a pharmaceutical point of view, it is of crucial importance to characterize the physical state of the encapsulated molecules as unexpected physical behaviors due to strong confinement effect were observed. In this contribution we propose an overview of the solid-state NMR characterization of such systems. In particular, we show how variable temperature experiments can precisely characterize the physical state of drug-model molecules including ibuprofen (a nonsteroidal anti-inflammatory drug) and alendronate (a drug preventing osteoporosis) confined in mesoporous silica materials such as MCM-41 or SBA-15. Moreover, a multinuclear study was developped to identify the specific interactions that take place at the molecule/silica interface. These lattest experimental results were confronted to periodic DFT calculations which were found to be reliable with the in vitro release behavior. Finally, the homoneneity of the materials was investigated by an original method namely the hyperpolarized 129Xe spectroscopy which permits to build a precise model of the molecules partition in the mesoporous matrix.

CB-8:IL02 Porous 1D Ceramics and Composite Ceramics via Electrochemical, Gas Phase and Precursor Routes

J.J. Schneider, Technische Universität Darmstadt, Fachbereich Chemie Eduard Zintl Institut Anorganische Chemie, Darmstadt, Germany

Porous ceramic materials have a wide impact in catalysis and sensing applications. If pore sizes and volumes of such ceramics can be adjusted and tailored in certain ranges such materials become interesting as new supports for catalysis or as porous catalysts itself. Using gas phase and solution techniques porous ceramic single phase materials can also be structured into more complex binary or even ternary porous composite ceramics with an overall hierachical structure. In this contribution we will report on the formation of ordered and unordered porous templates using electrochemical approaches and how such template materials can be used to synthesize highly arranged carbon nanotubes (CNTs), alumina reinforced CNTs, metal and ceramic reinforced CNTs using gas phase and solution approaches. In addition studies towards crystalline titanium dioxide nanotubes and amorphous and crystalline group 12, 13 and 14 nanorods and nanotubes will be presented. By templating appropriate precursor solutions onto/or into porous template structures, porous ceramic oxides of main group, transition metal or rare earth elements are accessible. Access to either endo or exoporosity depending on the templating synthesis pathway is thus possible.

CB-8:IL03 Hybrid Foams, Colloids and Beyond: Integrative Chemistry

R. Backov, CRPP-UPR CNRS 8641, Pessac, France

Today chemists are required to design and conceive architectures more and more complex regarding both their nature and texture enable to develop a certain degree of autonomy, mimicking for instance biological organisms. Such complex architecture's synthetic modes shall be addressed with a strong interdisciplinary approach of chemical science. In this overall context is emerging the new concept of Integrative Chemistry. Herein, we will show first how to engineer new hybrids or carbonaceous foams by combining concentrated emulsions, lyotropic mesophases and sol-gel process. Secondly we will describe how it is possible, when dealing with diluted emulsions, millifluidic, or Pickering emulsions to promote single objects as core-shell particles dedicated to for instance to thermo-stimulated drug delivery. Overall, enhanced applications as heterogeneous catalysis, electrochemical capacitors, enzyme made bio-sensors and thermo-stimulated drug delivery will be discussed.

CB-8:L04 High Surface Area Cr2O3 Tubes Synthesized by Replica Technique

P. Gibot, Institut franco-allemand de recherches de Saint-Louis (ISL), Laboratoire Nanomateriaux pour les Systemes Sous Sollicitations Extremes (NS3E), ISL/CNRS UMR 3208, Saint-Louis cedex, France

Chromium (III) oxide (Cr2O3) is known to be an interesting material for a lot of applications in very different research fields. For example, Cr2O3 is used as an electrode for gas sensors, catalysts in volatile organic compounds removal, optical absorptions, in pyrotechnic systems and negative electrode in lithium battery. Consequently, the preparation of this metal oxide with tailored properties such as a low particle size, well-defined shape (1 to 3D) and high specific surface area, is became primordial. In this communication, we describe an original replica method for the synthesis of high surface area Cr2O3 chromium oxide powder involving the use of chromium nitrate and carbon fibers or silica balls as chromium precursor and hard template materials, respectively. The conventional dip coat technique was used with the carbonaceous templates (ex-PAN, ex-Brai fibers). The fibers (chemically activated or not) were dip-coated in a chromium aqueous solution, dried at 100 °C and calcined at 550 °C under air. After the carbonaceous template removal, well-crystallized Cr2O3 powders with tube like-shape morphology and high specific surface area (>100m^2/g) was obtained with success.

CB-8:L05 Investigation on the Microstructure and Permeability of Porous SiC Ceramics

In-Hyuck Song*, Il-Min Kwon, Hai-Doo Kim, Korea Institute of Materials Science, Changwon, Korea; Young-Wook Kim, The University of Seoul, Korea

Porous silicon carbide (SiC) ceramics show unique characteristics such as low density, low thermal conductivity, high thermal shock resistance, high surface area, and high specific strength, which usually cannot be achieved in their conventional dense counterparts. For filters, vacuum chucks, and air spindle applications, the achievement of high gas permeability is a key factor in the development of porous SiC ceramics. However, very few reports on the gas permeability of porous SiC ceramics can be found in the literature. In this study, porous SiC ceramics were fabricated by Si bonded sintering process. In particular, hollow microspheres as the pore formers were added to create a cellular pore structure with high permeability. The effects of SiC particle size and sintering temperature on porosity and permeability were investigated. Although the porosity was over 60vol%, the bending strength of the specimen was about 50 MPa. The permeability of porous SiC ceramics could be controlled to some extent by adjusting the experimental parameters.

CB-8:L07 Synthesis and Characterization of Spherical Mesoporous Hydroxyapatite

F-.Y. Yeoh*, K-.S. Lew, School of Materials & Mineral Resources Engineering, Universiti Sains Malaysia, Nibong Tebal, Penang, Malaysia

Porous media such as silica, polymethyl metacrylate and polyethylene glycol have been studied for targeted drug delivery application. Among the porous media, Hydroxapatite (HA) possesses exceptional biocompatibility and bioactivity properties with respect to bone cells and tissues, due to its similarity with the hard tissues of the body. In present study, mesoporous HA was synthesized using a templating technique by self-assembly, which is analogous to the synthesis of mesoporous silica MCM-41. The co-precipitation method involved the precipitation of HA surrounding the hexagonal-phase micelle template formed by surfactant. After ageing, calcination was carried out to remove the templates as well as to produce more crystalline and more stable HA structure. Compared to other particle shapes (eg. needle and irregular shape), spherical drug carrier triggers the least immune reaction. Thus, spherical particle is more suitable for drug delivery application. Consequently, the particle morphology of mesoporous HA was controlled in the desired spherical shape using spray drying technique. XRD results showed that phase pure HA was successfully prepared through this method. Mesopores with size ca. 4 nm could also be observed in HA powder using a TEM before and after spray drying.

CB-8:L08 Fabrication of Porous Ceramics by Spark Plasma Sintering

P. Miranzo*, E. Garcia, M.I. Osendi, Institute of Ceramics and Glass (CSIC), Madrid, Spain

Porous ceramics have a wide range of technological applications, such as molten-metal filters, catalyst supports, exhaust gas particle filter for diesel engines or gas burners. In all these applications, the pore structure is a key parameter that affects many of the material properties, particularly those stress and flux-determined, i.e. mechanical properties and thermal/electrical conductivities. This paper deals with the fabrication of porous ceramics, concretely mullite and silicon nitride based materials, by spark plasma sintering (SPS). This method allows low temperature sintering that maintains the pore structure of the starting green compacts, which have been obtained by two different procedures. One is based on the stacking of beads obtained by flame spraying spray dried powders in water, and they can be described like ceramic spherical particles surrounded by a network of pore channels (20 - 30% of open porosity). The other one is based in the addition of fugitive polymer particles to the ceramic matrix and they are formed by small intergranular pores embedded by the matrix particles (porosities <10%). The thermal and mechanical properties of the SPS specimens have been analysed and discussed considering the particular microstructural features.

CB-8:L09 Structural, Mechanical and Filtering Properties of Porous Titania / Alumina Ceramic

A. Butlers*, R. Svinka, V. Svinka, Riga Technical University, Institute of Silicate Materials, Riga, Latvia

There are numerous applications for porous ceramic materials. Water filtration, molten metal filtration, filtration of exhaust gases, as catalyst carrier, various refractory applications etc. Most of the commercially available porous ceramic materials are produced using different pyrolysis techniques witch has some considerable disadvantages - as toxic fumes, leftover residues of organic precursors etc. In our research a lightweight refractory ceramic is produced by foaming a slurry of raw materials, using a gas formation technique similar to the one used in aerated concrete technology. The dependency of pore size, geomety and porosity on the initial properties of slurry are analysed. After the firing and mechanical preparation the properties of sintered ceramic (such as composition, thermal shock resistance, mechanical porperties etc.) are evaluated.

Session CB-9
Ultra-high Pressure Ceramics Synthesis and Processing

CB-9:IL02 Synthesis of New Diamond-like B-C Phases Under High Pressure and Temperatures

Li Chung Ming*, P.V. Zinin, S.K. Sharma, Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, HI, USA

The finding of the new diamond-like B-C phases is of fundamental importance as these will shed light on the nature of the bonding of the boron atoms in the diamond lattice. These phases are also potential high-temperature superconductors and their development will help understand the nature of high-temperature superconductivity. Recently, theoretical simulations of pressure- and temperature-induced phase transition in the B-C system demonstrated that the incorporation of B atoms into a diamond structure should not lead to a drastic distortion of the cubic cell of a diamond. The unit cells obtained in the phases predicted theoretically (i.e., 3.745 Å for cubic BC and 3.642 Å for nearly cubic BC3) are slightly larger than that of a diamond (3.5667 Å). We have carried out synthesis of a new class of diamond-like materials from the graphitic BCx phases over a wide P-T range in a laser heated diamond anvil cell at pressures up to 50 GPa and temperatures to 3000 K. In this presentation, we are to discuss evidence for novel cubic BCx phases synthesized under high pressure and high temperature (HPHT) conditions. Identification of the new phases was based on x-ray diffraction, Raman spectroscopy and electron microprobe studies.

CB-9:IL03 High-purity Boron Nitrides: Ultra-high-pressure Synthesis and Properties

T. Taniguchi, National Institute for Materials Science (NIMS), Tsukuba, Japan

Hexagonal BN (hBN) and cubic BN (cBN) are known as the representative crystal structures of BN. The former is chemically and thermally stable, and has been widely used as an electrical insulator and heat-resistant material. The latter, which is a high-density phase, is an ultra-hard material second only to diamond. Some progresses in the synthesis of high purity BN crystals were recently achieved by using Ba-BN as a solvent material at high pressure crystal growth. Band-edge structures (cBN Eg=6.2eV and hBN Eg=6eV) were characterized by their optical properties. The key issue to obtain high purity crystals is to reduce oxygen and carbon contamination in the growth circumstances. It should be emphasized that hBN exhibits attractive potential for deep ultraviolet (DUV) light emitter. On the other hand, synthesis of high purity cBN sintered body is an important subject for its application as machining tools. Fine-grained cBN sintered body was synthesized without any sintering agent at 10-12GPa regions. The resultant sintered bodies exhibit superior mechanical properties as cutting edge for ferrous materials. This result indicates that the newly developed cBN tool with ultra-fine grained structure is useful for the ultra-precision or precision cutting of ferrous materials.

CB-9:IL04 High-pressure / High-temperature Synthesis of Oxynitrides

H. Huppertz*, Institut für Allgemeine, Anorganische und Theoretische Chemie, Leopold-Franzens-Universität Innsbruck, Innsbruck, Austria; S.A. Hering, Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, München, Germany; C.E. Zvoriste, Technische Universität Darmstadt, Material- und Geowissenschaften, Darmstadt, Germany; I. Kinski, Fraunhofer-Institut für Keramische Technologien und Systeme, Dresden, Germany

In recent years, research on group-13 nitrides intensified for the industrial market and for technical applications, due to their remarkable physical properties. Wurtzite-structured gallium nitride (w-GaN), belonging to the group of semiconductor materials, is well-known in optical and electronic devices such as detectors, solid state laser facilities, and laser diodes, or for its high potential for blue and white energy saving LEDs (light-emitting diodes). This system was modified by the addition of oxygen, leading to the substance class of gallium oxonitrides. This class of compounds may show similarities to the well-explored aluminium oxonitrides, including their potential for industrial applications in analogy to the alon system. Recently, we were able to synthesize a crystalline sample of a spinel-type gallium oxonitride, wherefrom single crystals of a spinel-type gallium oxonitride could be isolated and reported for the first time[1]. Furthermore, in-situ diamond anvil cell (DAC) investigations and multianvil experiments led to new insights into the stability field under high-pressure/high-temperature conditions.

[1] *H. Huppertz, S.A. Hering, C.E. Zvoriste, S. Lauterbach, O. Oeckler, R. Riedel, I. Kinski, Chem. Mater. 2009, 21, 2101.*

CB-9:IL05 Synthesis of Superhard Nanocomposites by Microstructural Design

E. Kroke*, M. Schwarz, T. Barsukova, TU Bergakademie Freiberg, Institute for Inorganic Chemistry, Freiberg, Germany; D. Rafaja, C. Schimpf, TU Bergakademie Freiberg, Institute for Materials Science, Freiberg, Germany

For nanostructured ceramics such as Ti/Si/N-films unusual hardness enhancements are known to occur if the Si:Ti-ratio, oxygen content, and particle sizes are in a suitable range. We investigated bulk boron nitride nanocomposites which were synthesised using the multi-anvil-press technique (MAP) under high temperature and high pressure (>1000 °C / >10 GPa). The graphitic h-BN starting material yields composites containing cubic, wurtzitic and small amounts of graphitic BN. Detailed analysis (XRD, HR-TEM) of the phase amount, particle sizes and orientation of the crystallites to each other provides a model for the nano-structure. Partial coherence of the crystallites and an accumulation of defects in the hexagonal phase are suggested to be at least in part responsible for the ultra-hardness, which was reproducibly determined to be significantly above the hardness of c-BN single crystals. Further studies where devoted to the phase transformation mechanisms involving the three BN phases. We also prepared the above mentioned Ti/Si/N phases as bulk nano-composites via MAP. The precursor technique offers an attractive approach to such composites yielding amorphous starting materials. Phase transformations were investigated in-situ using synchrotron radiation.

Session CB-10
Other Nontraditional Processing Routes

CB-10:IL01 **Clay Aerogel Composite Materials**

David A. Schiraldi*, Matthew D. Gawryla, Saeed Alhassan, Department of Macromolecular Science & Engineering, Case Western Reserve Unviersity, Cleveland, OH, USA

Smectite clays can be easily combined with a wide range of polymers in a robust, freeze-drying process using water as solvent. This environmentally-friendly process can incorporate synthetic or agricultural polymers to product high performance, low density structures suitable for replacement of traditional polymer foams, wood and many other materials. Processing, structure, properties, applications as well as models describing their behaviors will be discussed.

CB-10:IL02 **Heterogeneous Sol-gel Systems - derived Ceramics**

O.A. Shilova*, I.V. Grebenschikov, Institute for Silicate Chemistry of RAS, St. Petersburg, Russia

Glass-ceramic materials are successfully applied to prepare products, which are capable to work in extreme conditions (a heat, radiation, aggressive liquids and gaseous fluids). One of ways of preparing glass-ceramic materials and coatings is a sol-gel technology. Heterogeneous sol-gel systems, synthesized by mixing sols and fillers of various dispersity (oxides, minerals, etc.), are usually used for their preparation. Sol composition (precursor, catalyst, solvent, dopants), filler dispersity and a homogenization mode for obtained suspensions essentially influence the properties of materials formed on their basis. Enveloping of filler particles and concluding them in a organic-inorganic polymer matrix are taken place during a sol-gel transition. This matrix after a heat treatment (at 450-900 °C) turns in glassy one. Thus, ceramic particles are fixed by thin and flexible layers of a glass phase. Such materials usually differ high reagent and spalling resistance, mechanical strength, and low porosity. In the report ways of controlling by properties of heterogeneous sol-gel systems (by using various dopants, additives of organic low- and high-molecular compounds, and ultrasound) to reach set electro-physical and mechanical characteristics of materials and coatings will be presented.

CB-10:IL03 **Smart Processing for Ceramics Structure Tectonics: Fabrication of Dielectric Micro Patterns for Artificial Photo-synthesis in Terahertz Wave Regions by Using Stereolithography**

S. Kirihara, Joining and Welding Research Institute, Osaka University, Osaka, Japan

Ceramics structure tectonics is new strategy of science and engineering to create novel functional materials with special patterns and morphologies. In this lecture, various investigations to develop the functionally structured materials by using smart processes of stereolithography will be introduced. For example, photonic crystals with periodic arrangements in dielectric constants are strong candidates of artificial functional materials to control electromagnetic wave energies effectively. Special modifications of dielectric micro patterns to harmonize electromagnetic waves in terahertz frequency ranges with molecule vibrations of various biochemical solutions will be introduced as investigative results of artificial photosynthesis.

CB-10:L04 **Chemical Approaches to Functional Nanostructures: Growth, Applications and Devices**

S. Mathur, Institute of Inorganic and Materials Chemistry University of Cologne, Cologne, Germany

Chemical design of inorganic materials deals with the transfer of short range chemical order, present in the molecular precursor state, to infinite correlation lengths in three dimensions. A generic chemical strategy based on the transformation of molecular precursors into functional inorganic nanostructures allows producing nanomaterials of different dimensions and morphologies with precisely controlled chemical composition and phase purity. The successful synthesis, modification and assembly of nanobuilding units such as nanocrystals, -wires and -tubes of different materials have demonstrated the importance of chemical influence in materials synthesis, and have generated great expectations for the future. Inorganic nanostructures inherit promises for substantial improvements in materials engineering mainly due to improved physical and mechanical properties resulting from the reduction of microstructural features by two to three orders of magnitude, when compared to current engineering materials. The chosen examples will include nanostructured functional films for hydrophobic, hydrophilic and barrier properties, application of superparamagnetic iron oxide nanoparticles for drug delivery applications, molecule-based synthesis of nanowires and development of single-nanowire based devices. This talk will focus how chemically processed nanostructures open up new vistas of material properties, which can be transformed into advanced material technologies. It will also address the several steps involved in the transformation of laboratory scale research into nanotechnology-based products and devices.

CB-10:L05 **Sintering and Mechanical Properties of Silicon Carbide Composites with In-situ Converted Titanium Oxide to Titanium Carbide**

D. Ahmoye*, V.D. Krstic, Queen's University, Kingston, Canada

Silicon carbide is an attractive structural material attributed to excellent mechanical properties that can be retained at high temperatures. Improvements to the hardness, strength and fracture toughness properties of SiC have stimulated interest for use in a number of industrial functions. Studies have shown that SiC containing a moderate volume fraction of dispersed titanium carbide improves flexural strength, fracture toughness and hardness. In the present study, SiC-TiC ceramics are prepared via an in-situ reaction of titanium oxide and carbon during sintering. Composites containing up to 30 vol% post-reacted TiC were pressure-less sintered with 4.7 wt% alumina and 5.3 wt% yttria to achieve maximum theoretical densities approaching 99%. Addition of TiC to the SiC matrix was shown to increase the fracture toughness and flexural strength relative to the amount of dispersed TiC present. Observations of the surface fracture paths indicate the improved mechanical properties are a result of the toughening mechanisms produced by the TiC particles.

CB-10:L06 **Processing of Municipal Solid Waste (MSW) Fly Ash into an Environmentally Stable and Safe Material**

M. Isac*, R.I.L. Guthrie, Z. Ghouleh, McGill University, McGill Metals Processing Centre (MMPC), Montreal, Canada

The purpose of this research was to design a processing route for the conversion of hazardous MSW fly ash into a glass- ceramic material, stable and safe for further industrial, structural, or ornamental applications. The process firstly consists in the transformation of a hazardous Municipal Solid Waste (MSW) fly ash into a vitreous material. Thermal analyses information was used to design the controlled heat treatment that further transformed this vitreous material into an environmentally safety composite. The final product obtained was a glass-ceramic material with randomly oriented crystals embedded in its residual amorphous matrix. The crystalline phases forming were identified as Nepheline and Diopside. Material's characterization and chemical analyses were carried out with the help of XRF, XRD, TCLP, SEM/EDS, DTA, TMA, Optical Microscopy, Confocal Laser Microscopy, and Vickers micro-hardnes. Improved mechanical properties, such as hardness, stiffness, toughness, and thermal shock resistance of the glass-ceramic composite were recorded. Fracture surface analysis was also performed for both materials, revealing that the vitreous material exhibits the characteristics of a brittle-type fracture, while the glass-ceramic displays that of a non-brittle-type fracture.TCLP (Toxicity Characteristic Leaching Procedure) was performed in accordance with US-EPA Method 1311. TCLP results were significantly lower than regulatory limits.

Poster Presentations

CB:P01 **Silica Tube Gel Manufactured by Electrolysis**

Nagakazu Furuya, University of Yamanashi, Takeda, Kofu, Japan

In general, granular silica gel is obtained from the addition of sulfuric acid to sodium silicate solution. However, manufacturing a tube shape silica gel is difficult. Then, manufacturing a tube shape silica gel using by electrolysis was tried. The tube shape silica gel can be obtained according to the shape of the anode. Moreover, the pore distribution of the silica gel can be easily changed by introducing an additive in the electrolyte solution. The electrodeposition of silica gel was made from $5mA/cm^2$ to $600mA/cm^2$. The range of the cell voltage was from 3.0V to 5.5V when 0.1~1.0mm platinum wire is used. Silica gel of a tube of 0.1~1.0mm in the inside diameter and 1~10mm the external diameter and 40mm in length was obtained by extracting the anode in the electrolyte. The measurement of the specific surface area and pore distribution of the silica gel was performed with a Porosimetry Analyzer TriStar 3000. Silica gel tube of 40mm was obtained though cracks formed when drying at 300 °C. We were able to control the specific surface area ($80m^2/g \sim 1080m^2/g$) and the average pore size (2.3 ~ 15nm) by adding a surfactant or various salts in the electrolyte.

CB:P02 Polyol Mediated Route of Porous Hafnium Oxide Nanostructures

M. Villanueva-Ibáñez*, M.-A Flores-González, Laboratorio de Nanotecnología y BioElectroMagnetismo Aplicado, Universidad Politécnica de Pachuca, Hidalgo, Mexico; M.-A. Hernández-Pérez, H.J. Dorantes-Rosas, Escuela Superior de Ingeniería Química e Industrias Extractivas, Instituto Politécnico Nacional, D.F., Mexico; H. Montiel-Sánchez, Grupo de Materiales y Nanotecnología, CCADET-UNAM, Mexico

Hafnium oxide has important physical and chemical properties; it is widely used in optical domain due to its high refractive index (≈ 2 for tetragonal phase). As porous material is barely studied in comparison with alumina, titania or zirconia. Nevertheless hafnium oxide is interesting because it has a low temperature phase (monoclinic) wich is very stable up to 1850 °C and a high chemical stability in the whole pH range. Hafnia is an attractive porous ceramic support for diverse applications like membranes for nanofiltration, catalysts supports and biofilms. Numerous methods have already been reported to prepare hafnium oxide. In this work, we report on the preparation and characterization of nanostructured porous hafnium oxide by an original synthesis. The material has been obtained from inorganic salts like hafnium chloride dissolved in dietilen glycol. Parameters of the reaction were regulated (acidity, temperature, reaction time) in order to have a control on the morphology of the final material. The HfO2 powders were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy and porosity analysis. The heat-treated samples present a monoclinic structure in all temperatures and the aggregates have nanoparticles of around 15 to 20 nm.

CB:P03 SiCN Xerogels and Ceramic Materials Derived from Polymers Containing vinyl- and Carbodiimide Functional Groups

H.J. Cheng, Y.L. Li, Y. Dai*, Key Laboratory of Advanced Ceramics and Machining Technology (Tianjin University), Ministry of Education, Tianjin, China; E. Kroke, M. Schwarz, Institute of Inorganic Chemistry, TU Bergakademie Freiberg, Freiberg, Germany; S. Herkenhoff, J. Woltersdorf, Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

SiCN xerogels were synthesized by polymers containing vinyl- and carbodiimide functional groups. Related ceramic materials were fabricated using this polymer precursor polysilylcarbodiimide pyrolysed at 1000 °C with NH3 atmosphere-assisted heating process. The microstructure, morphology and microchemistry of the xerogels and ceramic materials were investigated by different methods. SEM and HR-TEM images revealed that the SiCN ceramics pyrolysed in NH3 exhibit amorphous porous microstructure. FTIR spectroscopy showed the existence of main chemical bonds of Si-N and Si-C. In addition, N=C=N chemical group exists still in this ceramic materials even after 1000 °C pyrolysis observed in FTIR and NMR spectra. The pore size distribution was analyzed by mercury intrusion methods showing a broad distribution of pores in the ceramic body from nanometer to micrometer. The microstructure evolution of precursor-derived SiCN ceramics upon exposure at temperatures ranging between 1000 and 1500 °C has also been investigated. The results of the present study indicate that the materials convert from amorphous station to crystalline structure around 1400 °C. The presence of the localized crystalline regions was detected mainly composed of Si3N4 crystals and few graphitic carbons by EELs and XRD.

CB:P06 The Effect of Pulsing on the Spark Plasma Sintering of Silicon Nitride Materials

J. Gonzalez-Julian, P. Miranzo, M.I. Osendi*, M. Belmonte, Institute of Ceramics and Glass (CSIC), Campus de Cantoblanco, Madrid, Spain

The sinterability of most of the materials increases when the spark plasma sintering (SPS) technique is used, although the phenomena responsible for the enhanced sintering are still under debate. In the case of silicon nitride (Si3N4), dense materials with negligible grain growth and phase transformation can be attained, which could be explained by an improvement of the particle rearrangement stage during the sintering process due to the enhancement of the liquid phase wetting. In this work we shall get insight in this mechanism modifying the pulse pattern of the SPS process. Si3N4 compositions containing different amounts (2.5-7.0 wt%) of sintering additives were selected. SPS conditions were kept constant using a maximum temperature of 1600 °C for 5min, a heating rate of 133ºC.min-1, and 50MPa of uniaxial pressure. The pulse pattern was modified from 12:2 (12 pulses on, 2 pulses off) to 2:8. The effect of pulsing on the shrinkage curves, microstructure evolution, and α/β ratio was evaluated. The voltage per pulse increased as the ratio on:off decreased. Besides, the starting shrinkage temperature diminished and the particle rearrangement stage shifted to lower temperatures, enhancing the sintering kinetic of Si3N4 materials even for the lowest additives content composition.

CB:P07 The Effects of Codoping Y2O3 on MgO Doped Spark Plasma Sintered Al2O3

B. Apak*, F.C. Sahin, G. Goller, O. Yucel, Istanbul Technical University, Istanbul, Turkey

Nanocrystalline alumina (Al2O3) powders were sintered by Spark Plasma Sintering (SPS) in a vacuum atmosphere to obtain highly dense and fine grained final ceramic products. In the first section of experiments, 0.1% wt MgO doped Al2O3 is sintered at high temperatures and under high pressure with a SPS system. Later sintering procedures were carried out with codoping Y2O3 in order to investigate dopant effects on spark plasma sintered alumina. The microstructures of all samples were observed by scanning electron microscopy and the properties such as density, hardness and fracture thoughness were examined.

CB:P08 Spark Plasma Sintering of B4C-SiC Composites

H. Didem Genckan, Filiz Sahin Cinar*, Adnan Tekin Research Center of Materials Science and Production Technologies, Istanbul Technical University, Istanbul, Turkey

In this study, B4C/SiC composites containing %5, %10, %15 amounts of SiC were produced by spark plasma sintering of B4C, SiC powder mixture. B4C, SiC powder mixtures were prepared by using SiC balls in ethanol for 5 hours. Powders were sintered in to the graphite molds in SPS. Sintering process was carried out at different temperatures and under 40 MPa pressure in a vacuum atmosphere. After sintering process, the phase formation in the samples was measured by an X-ray difractometer. The variation in density, hardness, fracture toughness and microstructure of samples were investigated.

CB:P11 Crystal Growth of Calcite Nano-plates by Alternate Soaking Method, Using CDS Single Crystal Templates

K. Hayashi*, M. Tomohara, K. Fujino, G. Sakane, Y. Katayama, LSSC Okayama University of Science, Okayama, Japan

The alternate soaking method to synthesize multilayer polymer films was first reported by G. Drecher in 1997. T. Serizawa (2006) applied this method to the crystal growth of calcium carbonate on a multilayer polymer film. S. Mann (2001) reported the growth of calcite single crystals on the CDS monolayer film. In the present investigation, we grow the calcium carbonate nano-plates by the alternate soaking method, using the CDS single crystal templates. First, we grow the CDS single crystal templates of 1mm2x0.1mm. Second,the crystal structure of CDS is determined by single crystal XRD method,since the sulfate arrangement affects the orientation and the distortion of the growing calcium carbonate single crystal. The matching of calcium atom arrangements of the CDS template and the calcite crystal is estimated. Third, the nano-thick calcite single crystal growth is performed by alternate soaking in the calcium ion solution and the carbonate ion solution. The thickness of the crystal increases as the alternate cycle increases. The calcite single crystal grows in the (006) orientation to the sulfate surface of the CDS crystal.

G. Drecher, Science 277 (1997) 1232; T. Seizawa et al, J. Cryst. Growth, 292 (2006) 67; S. Mann, Biomineralization, 2001, Oxford press 171-174

CB:P13 Highly Porous Hydroxyapatite Ceramics for Engineering Applications

H. Ivankovic*, S. Orlic, D. Kranzelic, E. Tkalcec, University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia

Highly porous hydroxyapatite ceramics for engineering applications was produced by hydrothermal treatment (HT) of aragonitic cuttlefish bones. Mechanism of hydrothermal transformation of bones was investigated using DTA/TG coupled with FTIR spectroscopic gas cell (FTIR-EGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Bones were heat treated at 350 °C for 3 hours to remove organics, and successively hydrothermally treated at various temperatures and times. Aragonite monolits were completely transformed into hydroxyapatite at 200 °C 48 hours. In the samples with shorter HT, non reacted aragonite transforms during the DTA analysis into calcite. The decomposition of calcite is shifted to lower temperatures with treatment time. Evolved gas analysis has shown that incorporation of CO32- into hydroxyapatite structure depends on HT time and yields 1.2 - 1.5 wt% of CO2. SEM analysis shows that microstructure of cuttlefish bone was preserved after HT, retaining the same channel size (about 100x300 µm). On the surface of aragonitic monolits dandelion-like HA structures with diameter 3-8 μm were formed. With the prolonged HT treatment radially oriented nanoplates and nanorods were developed. The original porosity of bones was retained (~90%), while the specific surface area was increased from 2.5 to 8.5 m2/g.

CB:P14 **Aluminum Oxide Ceramics with Gradient Porosity Obtained by Commercial Starch Consolidation and Conformation**

R.P. Mota*, M.A. Algatti, DFQ-UNESP, Campus de Guaratinguetá, Guaratinguetá, SP, Brazil; R.S. Fernandes, Universidade Federal de Alfenas, Departamento de Ciencia e Tecnologia, Campus de Poços de Caldas; E. Campos, Escola de Especialistas da Aeronáutica, Guaratinguetá, SP, Brazil

The starch conformation and consolidation is a technique commonly used for obtaining porous ceramics. In this technique starch is used as a bonding and porous-maker element. In this process the slip is previously put in an impermeable mould where the gelling occurs. The main difference of the method adopted in this paper compared with the traditional one is that a mould with a plaster porous base was used (consistency of 70 and 90) improving the water drainage by action of gravity and the capillarity effect. Porous aluminum oxide ceramics were obtained from slips with 50% of solids in volume using as precursors aluminum oxide A-1000SG and commercial cornstarch with a mass concentration varying from 10 to 40%. For comparison between the present method and the common one slips were put in impermeable and permeable base moulds. The gelling occurred at 700 Celsius for 2 hours and the drying at 110 Celsius. Pre-sintering was carried out at 1000 Celsius and the sintering at 1600 Celsius with a plateau of 1 hour. Results showed that the plaster consistency of the mould bases was preponderant on ceramics porosity. Porosity and apparent density measurements using optical and electron-microscopy revealed variation of 5% of porosity from the top to the bottom of the samples.

CB:P15 **New Methodology in Modeling Ceramics Morphology**

M.A. Algatti*, R.P. Mota, FEG-DFQ-UNESP, Campus de Guaratinguetá, Guaratinguetá, SP, Brazil; E.C. Campos, E.F. Lucena, Escola de Especialistas da Aeronáutica, Guaratinguetá, SP, Brazil

The improvement of ceramic synthesis and processing methodology based on digital image processing and analysis of ceramic samples is in its initial stage. The main reason is that the models are based on poorly obtained data from sample's digital image processing. The lack of a solid statistical analysis and digital-imaging setup standardization make the method less useful that it should be if set in a sound basis. Therefore the importance of setting a new methodology in digital image processing for data acquisition on ceramic morphology analysis is essential for setting new models for customized ceramic synthesis and processing. The present paper shows results based on imaging by Scanning Electron Microscopy (SEM) of alumina ceramics obtained by pressing and starch consolidation methods. Observation of different sample's regions allowed a more accurate description of ceramic morphology. Plots of resistance to flexion versus porosity and its correlation with the grain size and shape allowed one to choose the best model for representing ceramic's morphology. Correlation of starch percentage with sample's porosity and mechanical resistance allowed the best experimental conditions for customized ceramic's performance.

CB:P17 **Preparation of Porous Silicon Nitride by Sacrificial Templating**

R.M. Mesquita, A.H.A. Bressiani*, L.A. Genova, Instituto de Pesquisas Energeticas e Nucleares, IPEN - CNEN, Sao Paulo, Brazil

High performance porous structural ceramics have been widely studied. Silicon nitride is an interesting material for this application because bodies with high mechanical strength, achieved as a result of "in situ" anisotropic grain grown, can be obtained. In this study, Si3N4 bodies with different porosity related aspects (percentage, size distribution, etc.) were obtained by changing the percentage (vol.%) and type of starch in the mixture as well as the sintering parameters. The porosity, apparent density (Archimedes method), microstructure (SEM) and the mechanical strength (in compression) of these bodies were determined. It was thus possible to relate the type and amount of starch with the porosity and mechanical properties of the bodies. The samples prepared using potato starch and rice showed the lowest and highest mechanical strength respectively.

CB:P18 **Influence of Binder on Porous Ceramic Properties Prepared by the Polymeric Sponge Method**

Katarzyna Jach*, Dariusz Kalinski, Marcin Chmielewski, Katarzyna Pietrzak Institute of Electronic Materials Technology, Warsaw, Poland

Porous ceramic materials are used in both medicine and industry. Porous ceramics can be prepared in the form of a filter element or a thermal insulator, or may be as a composite element. Preforms of this type may be application only if they meet the structural requirements imposed. In order to obtain the porous ceramic material the polymeric sponge method was applied. It is a method involving the deposition of the ceramic slurry onto polymeric sponge. The polyurethane sponge of 70%, 80% and 90% open porosity fabricated by the Kureta company was used. Ceramic porous materials obtained on the basis of alumina Almatis with an average grain size > 0.5 um. Aqueous suspension was prepared using two types of binders, poly(vinyl alcohol) and dispersion based on methacrylic acid esters and styrene. The aim of this study was to explain the relationship between the composition of the weight slips, the conditions of sintering and obtained porous ceramics structure. In this paper the results of studies on rheological properties of ceramic slurries and strength tests of ceramic materials are presented.

CB:P19 **Mechanical Properties of Si3N4 - SiC Composites Sintered by the HPHT Method**

P. Klimczyk, The Institute of Advanced Manufacturing Technology, Cracow, Poland

In recent years, there has been considerable interest in the mechanical properties of ceramic nanocomposites. Nanopowders could theoretically be easier to densify in comparison with conventional, microstructured powders. On the other hand, in practice, some common problems with densification of nanopowders are known. The large specific surface area of nanograins causes a tendency to absorb a high amount of different gases and impurities. These impurities often contribute to the cracking of sintered nanomaterials. Another difficulty in the consolidation of particulate nanostructured materials is ensuring complete compaction while retaining the nanocrystalline structure. In the present work three types: micro-, submicro-, and nanostructured Si3N4-SiC composites have been obtained by High Pressure - High Temperature (HPHT) sintering. Density, Young modulus, hardness and fracture toughness have been measured. A strong influence of initial powder size on mechanical properties of Si3N4-SiC composites can be observed. HPHT sintered materials obtained from submicron powders are characterized by better mechanical properties than those obtained from micro- and nanopowders. Submicro-Si3N4-SiC composites have better hardness and fracture toughness than comparable commercial ceramics

CB:P20 **Phosphate Bonded Alumina: Effect of Crystalline (AlPO4) Polymorph Phase Transformation on Mechanical Properties**

Pankaj Kumar*, A.N. Tiwari, Parag Bhargava, Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Powai, Mumbai, India

Alumina and alumina matrix composites typically require sintering temperatures in excess of 1550 °C. The present study was motivated from the possible process flexibility and energy saving owing to the reduced sintering temperature with use of phosphate bonding of alumina. Aluminum phosphates have been known for their good bonding ability as illustrated from their use in refractories, in providing oxidation resistant coatings on carbon-carbon composites and bio-ceramics etc. While phosphate bonded alumina is unique in the ways mentioned above, its limitations include the presence of porosity in pressure less sintered samples leading to lowered strength and phase instability above approximately 1200 °C.This paper describe the different processing routes, effect of AlPO4 binder concentration and its polymorphs on hardness (Hv), Young's modulus (E), Transverse rupture strength (S) and Compressive strength (s) of PBA. In this study, ultra fine Al2O3 (particle size ≈0.5 μm) was reacted with H3PO4, mixed with tabular alumina (particle size ≈5 μm, α-Al2O3), compacted at pressure in the range of 96 - 288 MPa and heat treated at different temperatures in the range of 500 - 1280 °C to yield phosphate bonded alumina. Samples of PBA with different porosity and AlPO4 polymorph bonding phase obtained through heat treatment at different temperatures were characterized for their mechanical properties. The mechanical properties exhibited by the sintered PBA were found to be in the range of Hv=360-480 kg/mm2, E = 134-140 GPa, S = 72-112 MPa and σ = 220-320 MPa at the optimized processing conditions.

CB:P22 **Reactive Milling and Mechanical Alloying in Electro-ceramics**

C. Gomez-Yanez*, I.A. Velasco-Davalos, C.A. Peralta-Zenteno, J.J. Cruz-Rivera, Department of Metallurgy and Materials Engineering, ESIQIE, National Polytechnic Institute, Mexico city, Mexico; Faculty of Metallurgy, UASLP, Sierra Leona 550, Lomas 2a. Seccion, San Luis Potosi, Mexico

The main advantages of reactive milling and mechanical alloying are the reduction of particle size, good homogeneity and phase formation or dissolution during milling, and these are desirable characteristics in the production of electroceramics. However, the use of high-energy milling devices to process electroceramics did not seem to be an option because of the possible contamination from milling media. Other question was whether the compensation mechanisms, activated during doping, were the same or not, between the conventional and mechanical alloying methods. This presentation is the summary of results about the application of either reactive milling or mechanical alloying in systems based on BaTiO3, Bismuth titanates and ZnO-varistor formulation.

CB:P23 Synthesis of High-Temperature Stable Anatase Titania Polymorph Through the Addition of La(III), Cu(II), Ba(II) and Sr(II)

Marina Moraes Leite[1], Flavio Maron Vichi[1], Edoardo Joaquim de Souza Vichi[2, 3], [1]Chemistry Institute, University of Sao Paulo, Sao Paulo, Brazil; [2]Chemistry Institute, State University of Campinas, Campinas, Brazil; [3]in memoriam

A series of modified titania powders were prepared following three different synthetic routes: sol-gel method, surfactant template method and combustion method. The titania powders were modified with 1, 5, and 10 mol percent La(III) and 1 or 5 mol percent Cu(II), Sr(II) and Ba(II). The resulting ceramic materials were heated to temperatures up to 700 °C. The X-ray diffractograms show an increase in crystallinity and rutile formation with increasing temperature, which is confirmed by the appearance of a narrow [110] peak at 2theta = 27.5 deg. For the samples modified with Ba(II), however, the formation of rutile is prevented even at higher temperatures, and only the anatase form is obtained (narrow [101] peak at 2theta = 25.4deg). Since the anatase polymorph is reported to have a higher photocatalytic activity, this can be an interesting route to the preparation of stable, high temperature titania photocatalysts. A decrease in surface area is observed for the samples heated at higher temperatures, due to the collapse of the pore structure. However, with increasing La(III) content, the decrease in surface area is less pronounced. When heated at 700 °C, the sample with 1% La(III) shows a decrease from 260 to 15 m2/g. For 10% La(III) the decrease is from 218 to 50 m2/g.

CB:P24 Lithium Disilicate Glass-ceramic Obtained by the Silica Extracted from Rice Husk

Felipe Antunes Santos*[1], Claudinei dos Santos[1], Durval Rodrigues Jr[1], Dolores Ribeiro Ricci Lazar[2], Dayane Faviero de Castro[1], Daltro Garcia Pinatti[1], Rosa Ana Conte[1], [1]EEL - USP (Escola de Engenharia de Lorena da Universidade de Sao Paulo), Sao Paulo, Brazil; [2]IPEN (Instituto de Pesquisas Energéticas e Nucleares), Brazil

In this work, lithium disilicate glass-ceramic and glasses based on the Li2O-SiO2 system has been investigated by substitution of the high-purity SiO2 starting powders by silica obtained from rice husk. Glasses were developed by the use of stoichiometric composition of 66%SiO2:33%LiO2, using SiO2 obtained by the chemical treatment of rice husk. The influence of SiO2 substitution on phase formation, microstructure, hardness and fracture toughness were determined and discussed. Investigations were carried out by means of differential thermal analysis; X-ray diffractometry and scanning electron microscopy. Amorphous and transparent glasses were obtained after melting. These glasses, presented Tg near to 480 °C and crystallization peak at 660 °C, in both compositions and Li2Si2O5 as crystalline phases after heat-treatment. The hardness (HV300gF) presented average values near to 425HV and 430HV for High-purity and rice husk silica powders, respectively. Fracture toughness measurements present results near to 2MPam1/2, for both compositions.

CB:P26 Microwave Synthesis of Silicon Carbide; Rapid Processing and Nanowire Formation

L. Carassiti[1]*, I. MacLaren[2], P. Dobson[3, 4], P. Harrison[4], D.H. Gregory[1], [1]WestCHEM, Dept. of Chemistry; [2]Dept. of Physics; [3]Dept. of Electrical Engineering; [4]Dept. of Mechanical Engineering, University of Glasgow, Glasgow, UK

SiC is an attractive candidate for many applications including: grinding materials, polishing pastes, wear resistant coatings, catalyst supports, filters for molten metals or hot gases, high temperature structural materials and as reinforcement in composites[1]. Conventionally synthesis is performed by one of three methods[2]: (1) Reaction of SiH_4 with gaseous hydrocarbons, (2) reaction between $SiCl_4$ and CCl_4 in the presence of hydrogen or (3) carbothermal reduction of SiO_2. Microwave (MW) synthesis presents a very promising route to many materials because it is fast, clean and energy-efficient[3]. Following our use of high power MW methods to produce refractory transition metal carbides[4-6], we demonstrate that it is possible to prepare phase-pure β-SiC in 2 minutes simply using a domestic MW oven. We also show that it is possible to tailor the microstructure of the carbides produced, from sintered ceramics to high aspect ratio nanowires <50 nm in diameter. Materials are characterised by Powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy and Selected Area Electron Diffraction (TEM / SAED) and thermogravimetric and differential thermal analysis (TG-DTA).

[1]*M.A. Sharif, H. Sueyoshi, J. Euro. Ceram. Soc. 2008, 28, 311;* [2]*M.J. Ledoux, C. Pham-Huu, Cat. Tech. 2001, 5, 4, 226;* [3]*T. Taguchi, N. Igawa, H. Yamamoto, S. Jitsukawa., J. Am. Ceram. Soc., 2005, 88, 459;* [4]*S.R. Vallance, S. Kingman, D.H. Gregory, Chem. Commun., 2007, 742;* [5]*S.R. Vallance, S. Kingman, D.H. Gregory, Adv. Mater., 2007, 19, 138;* [6]*S.R. Vallance, D.M. Round, C. Ritter, E.J. Cussen, S. Kingman, D. H. Gregory, Adv. Mater., 2009, 21, 4502*

Focused Session CB-11

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF CERAMICS

Oral Presentations

Session CB-11.1

New Methods for Investigation of SHS

CB-11.1:IL01 "Solution Combustion" as a Promising Method for the Synthesis of Nanoparticles

A.S. Mukasyan, Dept. of Chem. & Biomolec. Eng., University of Notre Dame, Notre Dame, IN, USA

Solution-combustion is an attractive approach to synthesis of nanomaterials for a variety of applications,including catalysts, fuel cells, and biotechnology. In this paper, several novel methods based on the combustion of a reactive solution are presented. These methods include self-propagating sol-gel combustion and combustion of impregnated inert and active supports. It was demonstrated that, based on the fundamental understanding of the considered combustion processes, a variety of extremely high surface area materials could be synthesized. The controlling process parameters are defined and discussed. Examples of materials synthesized by the above methods are presented. A continuous technology for production of nanopowders by using the solution combustion approach is also discussed.

CB-11.1:IL02 Thermal Explosion in the Synthesis of Ceramic Materials and Items

I. Gotman*, E.Y. Gutmanas, Faculty of Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel

Over the last decade a gradual shift from the basic to applied research has lead to the development of a number of unconventional SHS processes that allow simultaneous synthesis and consolidation of the inherently porous combustion products. Pressure assisted thermal explosion (TE) mode of SHS results in dense products in cases when the heat evolved during TE and pressure applied are sufficient for consolidation. Reactive Forging (RF) SHS/TE-based method has been developed: in RF, a self-sustained reaction is ignited in a reagent blend by rapid heat transfer from preheated press rams, and a moderate uniaxial pressure is applied while a sufficient amount of a liquid or very soft phase is present in the combustion product. Combined with the developed Short Distance Infiltration (SDI) approach, RF provides conditions for fabrication of interpenetrating phase in situ composites with binary (Al2O3, TiB2, TiC) or ternary (MgAl2O4, Ti3SiC2, Ti3AlC2, Ti2AlC) ceramic matrices, as well as well as intermetallic-ceramic and metal-ceramic composites (MgB2-Mg, Mg2Si-Mg, Ti/Nb-Al2O3, TiNi-Al2O3). Compared to traditional melt infiltration, SDI has the advantage of the considerably shorter infiltration distances (µm vs. mm/cm). SDI is based on the presence of low melting phases in the powder blend. Rapid heating of compacts above Tm followed by application of pressure results in squeezing the liquid phase into the pores which promotes SHS reactions and consolidation and results in dense products with fine homogeneous microstructures. The RF-SDI approach has also been successful in fabrication ceramic matrix-diamond grinding wheels, parts from machinable ternary ceramics and light armor tiles. RF approach can be used also for production of 3-D porous structures by diluting the blend with non-reacting spacers, that can be easily dissolved after SHS processing. Simultaneous synthesis and consolidation of reaction products employing pressure assisted SHS is a “green”, cost effective and thus perspective fabrication route of structural parts.

CB-11.1:L03 Microwave Activated Combustion Synthesis and Compaction in Separate E and H Fields: Numerical Simulation and Experimental Results

R. Rosa*, P. Veronesi, C. Leonelli, A.B. Corradi, Dipartimento di Ingegneria dei Materiali e dell’Ambiente, Universita degli Studi di Modena e Reggio Emilia, Modena, Italy; M. Ferraris, V. Casalegno, M. Salvo, H. Shaohua, Dipartimento di Scienze dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Torino, Italy

Microwaves (MW) at the ISM frequency of 2.45 GHz have been used to ignite the Combustion Synthesis (CS) of pressed ceramic and metallic powders mixtures, using a single-mode applicator (TE104). This configuration allows to study the separate effect of prevalent electric or magnetic field processing. A general overview of MW-materials interaction, with particular attention to the MW peculiarities of being absorbed selectively by the reactive powders and of transferring energy and not heat directly, will be presented, together with numerical simulation results. Microwave activated combustion synthesis (MACS) has been also applied to high temperature materials joining, with the application of a moderate pressure during the irradiation with electromagnetic waves to promote adhesion and to reduce the newly formed compounds porosity. Experimental results regarding the MACS of different systems and its applications to the obtainment of thick coatings as well as joints between high temperature ceramics will be discussed.

Session CB-11.2
Fundamentals of SHS

CB-11.2:IL01 Use of Electrothermal Explosion and Electrothermal Analyzer (ETA-100) for the Study of Kinetics of Fast High-Temperature Reactions in SHS-Ceramic Systems

A.S. Shteinberg*, ALOFT, Berkeley, CA, USA; A.A. Berlin, Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

Due to the lack of specialty kinetic methods and instruments, the kinetics of fast high-temperature (h/t) reactions in SHS-ceramic systems has not been adequately studied. We developed methods of non-isothermal kinetics and designed instruments to obtain information about reactions in a wide range of practically important temperatures and rates. The use of electrothermal explosion (ETE) allows studying SHS kinetics for some ceramic systems characterized by very short total reaction times (up to ~10 µs). In ETE, both samples pressed from powders and cylindrical samples made from tightly rolled foils were studied. The heating was accompanied by high-speed scanning of the non-stationary temperature field on the sample surface. Description of electrothermoanalyzer ETA-100 manufactured by ALOFT is given. Kinetic parameters of fast reactions for the temperatures up to 4000 K can be measured by ETE using ETA-100. New kinetic data for fast h/t gasless SHS yielding refractory carbides and borides of transition metals, silicon and boron carbides, refractory oxides and hard alloys are presented. At high-speed impact of the samples, the reaction rate constants were found to exceed the combustion rate constants by many orders of magnitude. The kinetic mechanisms of the corresponding fast reactions seem to be different. It is shown that SHS in ETE mode has a significant potential as a method for welding of refractory and dissimilar materials, production of coarse superabrasives, etc.

CB-11.2:IL02 Mechanoactivation of SHS Systems and Process

V.V. Kurbatkina*, E.A. Levashov, National University of Science and Technology “MISIS”, Moscow, Russian Federation; A.S. Rogachev, Institute of Structural Microkinetiks and Materials Science, Chernogolovka, Moscow region, Russian Federation

Now mechanical activation (MA) is widely used in SHS. As applied to SHS, MA means preliminary mechanical treatment of starting reagents or their mixtures leading to structural transformations accompanied by accumulation of energy in matter. Effect of MA includes more uniform distribution of reagents (especially important for multicomponent mixtures), comminution of reagents and hence elevated contact between particles, elevated concentration of defects in metal and non-metal reagents, increase of reactivity of SHS-mixtures. The question on a way of an estimation of contribution of MA on the increase in reactivity is very important. In the work various aspects of influence of MA on properties of SHS-mixes are considered and the technique of an estimation of contribution of MA is offered. For SHS, the most suitable parameters for evaluation of the MA efficiency seem to be the amount of released heat and change in the activation energy for formation of target product. Results of researches have shown that MA affects significantly combustion temperature and speed; character of distribution of combustion wave and composition/properties of synthesized products. Using preliminary MA of SHS-mixes allows to impact purposively on composition/properties of materials produced by SHS.

CB-11.2:L04 Simulation of Gasless Combustion of Mechanically Activated Solid Powder Mixtures

S.A. Rashkovskiy, Institute for Problems in Mechanics of the RAS, Moscow, Russia

The MASHS (Mechanically Activated Self-Propagating High-Temperature Synthesis) process is investigated intensively in many works. At present one-dimensional heterogeneous models of combustion of mechanically activated systems are developed and investigated. The goal of present work is developing and investigating of 3D model and method for direct numerical simulation of Mechanically Activated SHS systems combustion. The method under consideration falls into three stages. On the first stage, a simulation of mixture structure is performed. An analysis of the structure obtained in simulations is carried out. On the second stage, the thermal conductivity of solid powder mixture is calculated. On the third stage of simulation, the ignition and combustion of each particle of the mixture is considered with taking into account of heat exchange between contacting particles. The results of numerical simulations are represented dynamically and compared with the experimental data, obtained by high-speed digital recording of mechanically activated SHS systems combustion.

CB-11.2:IL05 Gasless Combustion: Physical Modelling of the Process

A.S. Rogachev, Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka Moscow region, Russia

Gasless combustion represents a novel approach to the synthesis of materials, including ceramics and ceramic-metal composites. This method is based on exothermic reaction, which occurs inside the raw heterogeneous mixture converting it into the product (material) with tailored composition and structure. The skill of materials production using gasless combustion synthesis is based on concordance of the reaction kinetics, head evolution and heat transfer, phase- and structure formation. Several methods have been developed in order to study mechanisms of all these processes. In this lecture, the most significant results of High Speed Digital Micro-video-Recording, Time-Resolved X-ray Diffraction using Synchrotron Radiation, Quenching of the Combustion Wave and other methods are considered from the viewpoint of their impacts in understanding mechanisms of the process at microscopic and macroscopic levels. It is shown how these experimental results are used for creation of micro-heterogeneous model of gasless combustion. The work is supported by RFBR, grant 07-03-00753.

CB-11.2:IL06 Modeling the Combustion Synthesis of Intermetallic Compounds

F. Baras*, F. Bernard, Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, Dijon Cedex, France

The strong reactivity of metallic powder mixtures allows to use combustion synthesis to produce intermetallic compounds. Combustion synthesis is associated with very complex phenomena both at the macroscopic and the mesoscopic scales like quasi-spin combustion, relay-race propagation, or layered micrometric patterns in the reaction product. On the one hand, we have to understand the role of processing parameters on the emergence of these phenomena. On the other hand, it is important to consider the reciprocal influence between the properties of the combustion front and the reaction processes at the particle level. During this lecture, we give an overview of the mesoscopic modeling of combustion synthesis. We first present the progress made in the understanding of macrokinetics of combustion in heterogeneous media. Next, we explain how the statistical treatment of experimental images allows to characterize the properties of the synthesis fronts. Finally, we introduce the modeling of the reactive mechanisms at the level of a single particle. This approach demonstrates how the specificities of the front propagation can modify the morphology and the chemical composition of the synthesized solid.

CB-11.2:L08 **Macrokinetics of Formation of Macrostructure of Product in SHS**

V. Prokofiev*, V. Smolyakov, Department of Structural Macrokinetics of Tomsk Scientific Center of Siberian Branch of RAS, Tomsk State University, Tomsk, Russia

On the base of mechanics of heterogeneous media a mathematical SHS model was built and investigated which describes formation of macroscopic product structure. Effective method of numeric model investigation was suggested, which considers zonal structure of combustion wave. Dynamics of structural formation from ignition stage up to exit to stable state combustion was considered. Calculated dependencies of stationary combustion rate, final porosity and relative expansion of burnt part of the sample according to its diameter size of particles of easily melting component, starting porosity and pressure of gas in pores were obtained. Comparison with experimental data was made. Change in characteristics of combustion wave in unstationary regime was analyzed. Structural oscillation, leading to stratification of porous sample in zone of synthesis products and to free-running combustion was revealed. Factors, defining the initiation of structural oscillations were defined. It was shown, that slight compression of the sample, compensating loosening action of gas, stabilizes combustion.

Session CB-11.3
SHS of Ceramic Powders

CB-11.3:IL01 **Composites Produced by SHS Method - Current Develop-ment and Future Trends**

J. Lis, AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Kraków, Poland

The basic stages of progress in composite materials from a scientific approach to promising and rapidly developing applications are discussed. The systematic review of different forms of composites prepared directly by SHS or by SHS-origin precursors is presented. Powders are usually the starting material for manufacturing of ceramic and a lot of attention has been paid to find new routes for synthesis powders in form of nano or micro particles. The present work is aimed at efficient and convenient powder processing by SHS as an important target for future composites technology. The use of SHS may bring a considerable development in ceramic technology, by enabling a manufacturing of sinterable, high-purity nano or micro powders. It can be demonstrated in different ceramic systems explored by the authors and co-workers using SHS e.g. (a) Si-C-N, (b) Ti-Si-C or (c)Ti-Al-C-N as well as Al-O-N and Si-Al-O-N. Rapid combustion conditions were successfully used to manufacturing composite powders and nanopowders suitable for preparing multiphase composite materials having controlled properties. It has been concluded, that the SHS technique has brought an important contribution to the ceramic processing and may be considered as perspective approach for nanomaterials engineering.

CB-11.3:IL02 **Carbon Combustion Synthesis of Ceramic Oxide Nano-powders**

K. Martirosyan, Dept. of Chemical and Biomolecular Engineering, University of Houston, Houston, TX, USA

The rapidly growing market demand for nanoparticles calls for cost-effective and environmentally friendly technologies for their large-scale production. We developed a new, simple, economical and energy efficient synthesis of nanostructured complex oxides from inexpensive reactant mixtures, referred to as Carbon Combustion Synthesis of Oxides (CCSO). In CCSO the exothermic oxidation of carbon nanoparticles generates a steep thermal reaction wave that propagates through the solid reactant mixture converting it to the desired complex oxide product. CCSO is a modified form of SHS that maintains the advantages of SHS and circumvents some of its disadvantages. Specifically, it enables a more economical synthesis of complex oxides. The carbon used in CCSO is not incorporated in the product and is emitted from the sample as a CO2. A large gas emission provides a convective cooling mechanism trough the sample that significant reduces local temperature and prevents product partial melting and particles growth. We produced several advanced oxide ceramics such as ferroelectrics multiferroics, fuel cell components, hard/soft ferrites, superconductors and others. CCSO does not require use of expensive fuel reactants and complex equipment and can be scaled up for continuous mass production.

CB-11.3:L04 **Double SHS of W2B5 Powder from CaWO4 and B2O3**

Sertac Yazici, Bora Derin*, Metallurgical and Materials Engineering Department, Istanbul Technical University, Maslak, Istanbul, Turkey

In this study, production of tungsten boride compounds by self-propagating high-temperature synthesis (SHS) from CaWO4, Mg and B2O3 mixture and followed by HCl leaching was carried out. In the first stage of SHS reaction, molar composition ratio of WO3:B2O3:Mg mixture was selected as 1:2.5:8, and its adiabatic temperature value was estimated to be approximately 2045 °C. In the first leaching step, the SHS product was leached with aqueous acid solution (5.7 M HCl, 1/10 S/L, 1 hour, 80 °C) to eliminate MgO, Mg3B2O6 and Ca3(BO3)2 phases. The first leached product was consisted of WB, W2B5, W, W2B phases. In the second stage SHS process, the first leached product was reacted with the same amount of Mg and B2O3, and then the product was leached with aqueous acid solution (4.06 M HCl, 1/10 S/L, 1 hour, 80 °C). The chemical composition of the leached Double SHS product was found to be 99.3% wt. W2B5 and 0.7% wt. WB.

CB-11.3:IL05 **Regulation of Crystallites Size in Ceramic SHS**

S.L. Kharatyan, Institute of Chemical Physics NAS RA, Yerevan, Armenia and Yerevan State University, Yerevan, Armenia

Regulation of particle size is a challenging problem for SHS of ceramic materials. It comes through the fact that owing to the high temperature of SHS, in most cases the primary formed small particles grow as a result of secondary structure formation. By now several approaches were developed to control the microstructure of ceramic materials, particularly to synthesize nanomaterials. Among them are noteworthy the following: a) SHS with intensive gas evolution during the synthesis reaction, b) molten salt assisted combustion synthesis, c) chemically activated combustion synthesis, d) thermal dilution with decreasing the combustion temperature, e) solution or impregnation-solution combustion synthesis, f) partial reaction between initial powders before the SHS which reduces the adiabatic temperature and hence the product particle size, g) mechanical activation of green mixture with increasing the reactivity of the reagents and allowing to perform CS even for low exothermic systems yielding products with smaller particles, h) application of initial reagents with various particle size, particularly nanosize ones, etc. In the work the main attention is given to the first three approaches as well as to the studies performed in particle level by electrothermography.

CB-11.3:L06 **Production of Zirconium Diboride Powder by Self Propagating High Temperature Synthesis**

Burcu Akkas*, Murat Alkan, Onuralp Yucel, Metallurgical & Matls Eng. Dept., Istanbul Technical University, Istanbul, Turkey

In this study, the self propagating high temperature synthesis of zirconium diboride powders followed by acid leaching was carried out by using domestic H3BO3 raw materials. In the first stage SHS experiments, technical grade ZrO2 powder with different amounts of B2O3 obtained through fusing of H3BO3 at 1073 K for 2 hours and magnesium powders were used. The SHS products were resulted in the mixed of the ZrB2, MgO and unreacted ZrO2-B2O3-MgO forms. In the leaching step, the SHS products were leached in acid solution to remove impurities such as MgO and (Mg,Zr)O2. The effect of acid concentration on the selective leaching was studied at different concentration range, solid/liquid (S/L) ratio, and temperature. After the hydrometallurgical treatment, submicron sized zirconium diboride powder was obtained. The obtained products were characterized by using X-ray diffraction, chemical analysis and SEM techniques.

CB-11.3:L07 Combustion Synthesis of Tungsten Containing Ceramic Materials

Kh.V. Manukyan[1, 2]*, S.L. Kharatyan[1, 2], R.A. Mnatsakanyan[2], A. Zurnachyan[2], A. Voskanyan[1], V. Danghyan[1], [1]Yerevan State University, Yerevan, Armenia; [2]A.B. Nalbandyan Institute of Chemical Physics NAS, Yerevan, Armenia

Combustion reactions in the WO3-Mg-C, WO3-Mg-Si and WO3+SiO2+Mg highly exothermic systems are investigated. Process conditions which have influence on the combustion features and characteristics of materials are found to be preparation way of green mixtures, reagents ratio, amounts of additives used, pressure of inert atmosphere etc. Controlling these parameters allows to synthesize tungsten carbide (WC) and silicide (WSi2) and WC(W2C)-C catalyst nano-powders. The morphology of synthesized powders is strongly depending on the way of initial mixtures preparation. Particularly, initial mixtures prepared from the impregnation of high carbon or silica powders by tungsten containing solutions (peroxo-complexes of tungsten oxides, ammonium tangstate, etc.) result in formation of nano-powders with sizes of 50-300 nm and high specific surface area average 50-60m2/g. The catalytic activity of tungsten carbides-carbon materials are investigated in the conversion of isopropanol. High degree (80-100%) of selective conversion of isopropanol to the propylene at the lower temperatures (100-150 °C) is observed.

CB-11.3:L09 Catalyst-induced Vapor-solid Growth Route for Synthesis of B_4C Nanostructures: Nanobelts, Platelets and Whiskers

Serim Ilday[1], Erman Bengu[2]*, [1]Graduate Program of Materials Science and Nanotechnology, Bilkent University, Ankara, Turkey; [2]Department of Chemistry, Bilkent University, Ankara, Turkey

We report synthesis of low-dimensional B_4C structures using sodium-containing compounds through a modified carbothermal route under flowing atmosphere without the use of transition metal catalysts. A variety of nanostructures, including whiskers, belts, platelets, and particulates have been observed in the final product. Chemical and structural analyses of the final products have been made via Raman spectroscopy, XRD, SEM, and EDS. Carbon-to-sodium weight ratio in the precursor mixture is found to be a strong parameter in controlling the final morphology of the B_4C. This effect is consistent with vapor-solid (VS) mechanism of growth, where local concentration of gaseous B_2O_2 is controlled by the relative amounts of carbon and sodium in the reactor.

Session CB-11.4

Direct Production of SHS Products and their Characterization

CB-11.4:IL01 Advances SHS-Ceramic Materials for Surface Engineering Technologies

E.A. Levashov*, V.V. Kurbatkina, Yu.S. Pogozhev, A.E. Kudryashov, National University of Science and Technology “MISIS”, Moscow, Russia

Recent results on synthesis of advanced targets for magnetron sputtering (MS) are presented. Characterization of multifunctional nc- thin films and coatings deposited by MS were carried out. The second part of talk is devoted to nanostructured electrodes which are used in pulse electrospark deposition (PED) and chemical reaction assisted PED (CRAPED). Two groups of electrodes are presented: 1- dispersive-hardening ceramics DHS with effect of simultaneous strengthening of carbide grains and binder resulting precipitations; 2- disperse-strengthened ceramic with modified structure produced using focused alloying by nanosized refractory compound while affected the process of melt containing structure formation and lock the recrystallization. Composition and structure of carbide grains and intergranular phase in DHC just after SHS are not in equilibrium: supersaturated solid solutions are formed because of high temperature gradient and combustion velocity. Precipitates are formed resulting from concentration separation of supersaturated solid solution.

CB-11.4:IL02 Self-propagating High-temperature Synthesis of Iron- and Copper-matrix Cermets

Andreas Chrysanthou, School of Engineering and Technology, University of Hertfordshire, Hatfield, UK

The presentation will report on the adoption of two different approaches based on self-propagating high-temperature synthesis (SHS) to produce cermets. The first of these concerns the formation of the solid solution carbide, (Ti,V)C, of various compositions in an iron matrix by starting with elemental powders. It was observed that two types of carbide particles were generated within the matrix; a (Ti,V)C carbide of submicron size and a TiC-rich carbide of slightly higher size. Comparison of SHS Fe-TiC products showed that the addition of vanadium led to refinement of the carbide dispersions. The mechanism of formation of Fe-(Ti,V)C cermets will be discussed using chemical thermodynamic analysis. The second SHS approach involves the reaction between titanium and graphite by dropping compacted powders into a copper melts at 1250°C. The process yielded dispersions of TiC within the matrix as well as graphite flakes. The reaction mechanism will be discussed and the potential of SHS to yield dispersions within metal matrices will be assessed.

CB-11.4:L03 Combustion Synthesis of SiAlON Ceramics

K.L. Smirnov, Institute of Structural Macrokinetics and Materials Science, RAS, Chernogolovka, Moscow Region, Russia

SiAlON ceramics due to high strength, wear and corrosion resistance is a promising structural material for various fields of up-to-date engineering. According to this the developing of advanced methods for production of SiAlON ceramics is promising task of up-to-date materials science. The aim of the present work is to investigate the regularities of infiltration assisted combustion synthesis SiAlON ceramics. The main factors affecting the density, phase composition and microstructure of SiAlON ceramics synthesized are revealed experimentally: nitrogen pressure in the reactor, bulk density, composition and dispersity of initial reaction mixture. Nitrogen pressure about 10 MPa was used for obtaining of porous SiAlON ceramics such as membrane and catalyst support and for synthesis of SiAlON powders with desirable phase composition and with wide range of microcrystal morphologies: from agglomerates of nanosized particles up to large millimetric whiskers. Nitrogen pressure about 100 MPa was used for synthesis of high-density SiAlON-based composites: machinable SiAlON-BN, wearproof SiAlON-TiB2, conducting SiAlON-TiN and corrosion-resistant SiAlON-SiC ceramics. The properties of thus obtained composites are presented.

CB-11.4:L04 Sintering of Ti2AlC Powders Obtained by SHS Process

L. Chlubny*, J. Lis, M.M. Bucko, AGH-University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Technology of Ceramics and Refractories, Cracow, Poland

Some of ternary materials in the Ti-Al-C system are called MAX-phases and are characterised by heterodesmic layer structure. Their specific structure consisting of covalent and metallic chemical bonds influences their semi-ductile features locating them on the boundary between metals and ceramics, which may lead to many potential applications, for example as a part of a ceramic armour. Ti2AlC is one of this nanolaminate materials. Self-propagating High-temperature Synthesis (SHS) was applied to obtain sinterable powders of Ti2AlC Utilization of heat produced in exothermal reaction in adiabatic conditions to sustain process until all substrates are transformed into product is one of the advantages of the method that result in low energy consumption and low cost combined with high efficiency. Different substrates were used to produce fine powders of ternary material. Phase compositions of obtained powder were examined by XRD method. Than selected powders were used for sintering in various temperature both in a presureless sintering and hot-pressing process, in argon atmosphere. Properties and phase composition of obtained products were examined.

CB-11.4:IL06 Catalytic Properties of SHS Products

G.G. Xanthopoulou, Institute of Materials Science, "Demokritos" National Center for Scientific Research, Athens, Greece

Catalytic properties of SHS catalysts have been examined in different processes: oxidation of CO, H2, soot, hydrocarbons, organic acids, aldehyds, alcohols, deep methane oxidation, dehydrogenation, pyrolysis of diesel fuel, naphtha and petrol, oxidative dehydrodimerization of methane, hydrogenation, isomerization, cracking, production of synthesis gas, synthesis ammonia and other processes. In many cases the activity of the SHS materials is substantially better than commercial catalysts and some of SHS catalysts are already used in industry. The reasons responsible for the high activities measured for SHS catalysts are believed to be related to both the actual composition of the SHS products as well as the highly defective structure of the new materials due to the very high cooling rates. The high activity of these catalysts is even more remarkable as their specific surface area is much lower than that of traditional catalysts, offering the possibility of further enhancement of their activity by optimizing their porosity. Oxide SHS catalysts such as Cu-Cr-O have shown great promise for oxidation of carbon monoxide. It appears that SHS catalyst materials are at least as efficient at oxidizing carbon monoxide than noble metal systems, without the limitations, high cost, scarcity and processing difficulties inherent in the case of the traditional supported noble-metal systems. Other work showed that SHS materials containing manganese or copper display catalytic activity for the oxidation of soot contained in emissions from engines and factories. The catalytic properties of a range of complex oxide ceramics of general formula LnxMeyCuzO (Ln=La,Y,Bi; Me= Ca, Ba,Sr) prepared by the SHS method in the process of oxidative dehydrodimerization of methane to form C2-hydrocarbons have been studied. Modified Me-Mg-Al-O spinel catalysts for the pyrolysis of diesel fuel for the production of industrial gases and liquids, have also been developed by SHS. Mg-Fe-Cr-Al-O based SHS catalysts demonstrate very strong dehydrogenation function during pyrolysis of diesel fuel. Iron containing oxide SHS catalysts are very active in the process of dehydrogenation of gasoline and octane. The supported catalysts prepared by direct combustion method LaFe0.6Ni0.4O3/Al2O3 was tested in the auto-thermal steam reforming reaction of heavy hydrocarbon. Full conversion (100%) of JP-8 surrogate was maintained during the duration of the experiments (12 hours) and hydrogen concentration was close to the thermodynamically predicted theoretical limit (42 vol. %). Ni-Al intermetallic, oxides and spinel compounds as well as a Ni-on-carrier system, were synthesized using SHS. Ni-skeleton catalysts were very active in the hydrogenation processes. Thus, the SHS method has been used successfully for the development of very active low-cost catalysts for various applications.

CB-11.4:IL07 **Self-Propagating High-Temperature Synthesis of Cast Ceramics: Phenomenology, Mechanisms, Applications, and Practical Implementation**

V.I. Yukhvid, Institute of Structural Macrokinetics and Materials Science, RAS, Chernogolovka, Moscow region, Russia

Self-propagating high-temperature synthesis of cast refractory inorganic materials, items, and protective coatings (SHS metallurgy) is one of most promising directions of SHS research and development. SHS metallurgy is based on the combined use of metallothermic (thermit) reactions and conventional SHS from the elements. High combustion temperatures (3000-4000 °C) and intense melt splashing during combustion generate a need for carrying out the synthesis under gas pressure or in centrifugal machines in order to control the processes of combustion, structure formation, and product properties. The most important results obtained for over the past three decades can be summarized as follows: (1) Experimental and theoretical studies on high-temperature liquid-phase reactions in thermit-type multicomponent mixtures shed light on the mechanism of liquid-phase dynamics in these systems and on the effects of gravity, microgravity, and centrifugal forces on their combustion; (2) A number of means for regulating the composition and structure of cast materials have been elaborated, such as direct and inverse phase segregation to fabricated layered or functionally graded materials, the size composite constituents and controlling their composition, and preparation of amorphous nano-grained materials; (3) Liquid-phase SHS processes have been utilized to fabricate (a) a number of new hard and heat-resistant alloys and items made thereof (including lined tubes for transportation of abrasive/aggressive media and high-temperature melts); (b) oxide materials for use in abrasive tools and cast molding equipment; and (c) protective coatings of machine parts operating in conditions of intense wear and elevated temperature. The presentation will be addressed to the most important contributions to the development of SHS metallurgy made by the researchers and engineers from Russia, Japan, China, Italy, USA, France, etc.

Session CB-11.5

Industrialization and Application of SHS Ceramics

CB-11.5:IL01 **Mass-forced SHS Technology of Ceramic Materials**

O. Odawara, Tokyo Institute of Technology, Nagatsuta, Yokohama, Japan

SHS technologies are characterized by high-temperature generation, spontaneous reaction propagation and rapid synthesis. Our research and development on simultaneous synthesis and sintering has progressed by applying mass force effects to SHS technologies; metal-ceramic composite pipe formation with centrifugal force on thermite reactions(Centrifugal-thermite Process) and fine ceramic composite synthesis under microgravity formed with a free-fall, parabolic flight and sounding rocket. The Centrifugal-thermite Process has successfully attained to produce long ceramic-lined pipes(>3m), which significant feature for the production of long ceramic-lined pipes is mainly in its reaction propagation under centrifugal effect as well as the centrifugal force and reaction heat; the reaction first proceeds rapidly along the inner surface of the reactant and then in the radial direction, resulting in a homogeneous quality in the direction of pipe length. In the latter, the TiB2-Al composite synthesis by a free fall, for example, has made clear that the lack of mass migration and the improvement of wetting between TiB2 and Al under microgravity affect the formation of a fine and dense cermet-like structure in the products. An advanced approach on the mass-forced SHS technologies performed is introduced by designing product densities and SHS reaction system.

CB-11.5:IL02 **Development and Industrialization of Nano Materials (Metal and Ceramic) by SHS Process**

Chang Whan Won, Advanced Nanomaterial Depertement, Chungnam National University, Daejeon, South Korea

Refractory metal and carbide nanopowders (W, Ti, Ta, WC, W2C, TiC, TaC, etc.) have been the subject of interest for the past two decades in order to manufacture compact materials with dramatically improved mechanical properties for aerospace, military, chemical and metallurgical applications. The interest in nanomaterials has led to the development of many synthetic methods for their fabrication. In this paper the challenges, synthesis methods and the characteristics of refractory metal nanopowders of IV-VI sub-group of the periodic table are discussed. Special attention is paid to salt-assisted combustion reaction (SACR) as a promising technique for the large-scale production of refractory metal nanopowders. SACR is a promising and cost-effective manufacturing approach to produce high purity refractory metal and carbide nanopowders at a low cost. All research results were obtained by the combustion of MeOx (here Me is W, Ti, Ta, etc.)+Reduction agent (Mg, Zn, NaBH4, etc.) + C (black soot) reactive mixture diluted with alkali metal halide (NaCl, NaF, NaJ, etc). As a result nanosized metal and carbide particles with mean size between 20 and 150 nm were formed.

CB-11.5:IL03 **SHS Refractory Materials Furnon and their Practical Implementations in Kazakhstan and Russia**

Z.A. Mansurov, Al-Farabi Kazakh National University, Almaty, Rep.of Kazakhstan

The simplest refractory materials are mortars, i.e. refractory masonry mortars. The “Furnon” refractory mortars are elaborated and produced by the Combustion Problems Institute using SHS technology. The lining heating up to 1023-1373 K temperature on the working surface of thermal unit results in self-ignition of joints burning down to 45-50% lining depth in case of vertical joints. The combustion wave is extinguished from the back of the lining due to heating temperature decrease and heat toss increase in the brick works. The unique property of the “Furnon” mortars is manifested by effect of brick-works “welding” in single whole monolith. At the same time the “Furnon” SHS mortars being equal to the best traditional high-alumina and magnesial mortars in refractoriness rates, they prove their superiority over them in high temperature strength of brick binding. At 1673 K temperature the binding strength of usual mortars achieves 5-7 MPa while the same feature of the “Furnon” mortars being up to 12-15 MPa. The “Furnon” SHS mortars are widely used in repairs of rotary kilns of many productions. They are: Karaganda cement plant (Kazakhstan), OJSC “Vanadium-Tulachermel” (Russia). OJSC “AVISMA-Titanomagnievyi Combinate” (Russia), coke roasting furnaces of Omsk Refinery (Russia). Positive experience in applications of “Furnon” mortars for linings of transportation and vacuum ladles is accumulated in Bratsk aluminium smelting plant (Russia).

CB-11.5:L04 **On Isolation of Tc into Matrices Using SHS Process**

S.V. Yudintsev*, IGEM RAS, Moscow, Russia; E.E. Konovalov, IPPE, Obninsk, Russia; A.V. Kuprin, Moscow, Russia

Long-lived Tc-99 is one of the most dangerous fission products due to high solubility of Tc(VII) in water. In the spent nuclear fuel Tc exists mainly alloyed with Mo, Ru, Rh, Pd. An important task is to develop ways for management of Tc extracted from the liquid reprocessing waste. To immobilize Tc cements, alloys and ceramics are proposed, the best of which accommodate high content of Tc and possess corrosion durability. The main problem of synthesis of matrices is volatility of Tc(VII) and necessity of stabilization of Tc(IV), suitable for encapsulation in titanates due to substitution for Ti(IV) with a similar radius. To achieve the oxidation state, synthesis is performed by hot pressing (cold pressing

- sintering) in inert gas media and sealed containers. Such processing complicates industrial application. As alternate way for fabrication of the matrices for Tc-99 isolation technology via SHS (self-sustaining high-temperature synthesis) is suggested. The formation of the phases during SHS proceeds for a very short time, decreasing the loss of elements due to evaporation. Other ways to reduce release of Tc are achieved by introduction of Tc into initial batch not as Tc2O7 but in sorbed form with TiO2 or as TcO2 with a higher melting point and lower tendency for vaporization.

CB-11.5:IL05 **Development of Science Intensive Production Based on Important Scientific Discoveries**

A.G. Merzhanov, ISMAN, Chernogolovka, Moscow region, Russia

The idea of practical realization of the scientific discovery of solid flame combustion is discussed. It is well known that the important discoveries (such as laser emission, low-temperature plasma, etc.) find their practical application in everyday life and become essential in engineering, industry and economy. Any production based on the scientific investigation is called science intensive production. Their proper organization and application require a very deep knowledge of the scientific or technological backgrounds as well as thorough analysis of the market and technological conditions. The author regards the organization of large-scale centers (scientific facilities) as a strategic solution of the problem. In these centers besides the investigation of new technologies, equipment, materials, and their application in different areas, such important steps as practical approbation of the obtained achievements, staff training, and market analysis would be studied. Organization of such centers is considered for realization of the phenomenon of solid flame which appeared to be a scientific background of the promising method of Self-propagating High-temperature Synthesis.

CB-11.5:IL06 **Past and Current Accomplishments in Production of Ceramic Powders and Structures by Self-Propagating High-Temperature Synthesis Method**

Jan A. Puszynski[1]*, Alan Degraw[2], [1]South Dakota School of Mines and Technology, Rapid City, SD, USA; [2]Advanced Material Technologies, Inc., Morristown, TN, USA

A comprehensive review of both past and current world-wide accomplishments in the area of combustion synthesis, with special emphasis on the production of oxide and nonoxide ceramic powders, will be presented. This review will focus on scale-up and production initiatives undertaken by international companies and institutions. A significant part of this presentation will be dedicated to manufacturing of dense and porous structures involving combination of self-propagating high-temperature technique with other processing methods. Finally, new initiatives and challenges associated with this novel synthesis technique will be discussed.

CB-11.5:L07 **Porous SHS - Ceramics**

Yu.M. Maksimov[1]*, A.I. Kirdyashkin[1], V.K. Baev[2], A.N. Guschin[1], [1]Department for Structural Macrokinetics of Tomsk Scientific Centre SB RAS, Tomsk, Russia; [2] Khristianovich Institute of Theoretical and Applied Mechanics, Novosibirsk, Russia

Based on complex investigations, interrelation between the structure formation of porous ceramics and thermal conditions of SHS wave was revealed. Experimental - industrial works testing various functionality of produced porous products have been carried out. Metalloceramic filters such as Al_2O_3, SiO_2, Ti, Si, C to filtrate liquid and gases were obtained by SHS. Based on intermetallic systems, functional burners converting energy from gas burning into radiant heat energy have been developed. At present, the radiant burners with a capacity of 2000 kW are used in gas boiler rooms and allow saving up to 10% of gas. Porous SHS products from metal oxide composites have shown high affectivity by using them as block catalysts to convert chemical natural gas into synthesis - gas with a conversion level of 95%.

Poster Presentation

CB-11:P02 **Utilization of NbC Nanoparticles Obtained by Reactive Milling in the Production of Alumina Niobium Carbide Nanocomposites**

V. Trombini *, A.H.A Bressiani, Instituto de Pesquisas Energeticas e Nucleares, Sao Paulo, SP, Brazil; E.M.J.A. Pallone, USP, Faculdade de Zootecnia e Engenharia de Alimentos, Pirassununga, SP, Brasil; R. Tomasi, UFSCAR- DEMa Sao Carlos, SP, Brazil

The great interest for nanostructured materials is due to the improvements on the mechanical properties of final products. The same ones present a significant increase on the properties as hardness, wear and, in some cases, strength and toughness, when compared to monolithic ceramic. These improvements attracted attention of ceramic cutting industry, because better cutting tools can lead to an increase in production. In this work reactive high-energy milling, which can lead to self-sustaining reactions (SHS), was used for synthesis of NbC nanoparticles. The reaction products were desagglomerated and mixed with commercial ultra-fine alumina powder, producing alumina matrix nanocomposites with 5vol% of nanometric NbC. These nanocomposites was characterized physical, microstructural and mechanically. Results shown that is possible to obtain nanocomposites, with high densities and high values of hardness, from the powders obtained by reactive milling.

Focused Session CB-12

LAYERED AND FUNCTIONALLY GRADED MATERIALS

Oral Presentations

Session CB-12.1

Layered and Graded Materials, Composites and Hybrids

CB-12.1:IL01 **The Potential of Spark Plasma Sintering (SPS) Method for the Fabrication on an Industrial Scale of Functionally Graded Materials (FGMs)**

M. Tokita, NJS Co., Ltd., Yokohama, Japan

The Spark Plasma Sintering (SPS) Method is a solid compressive and pulsed electric current energizing sintering technique, that has lately drawn considerable attention as one of the newest rapid sintering method with excellent energy density control and capable of producing homogeneous Functionally Graded Materials (FGMs), nano-structural sintered compacts, thermoelectric materials and Bio-materials, in short time. Today in Japan, a number of SPSed products for different industries have already been realized. Although the SPS technology still involves an unclear fundamental mechanism portion, the cost reduction technology are currently making progress. Therefore, the SPS is now moving from academia and/or R&D proto-type product level to practical industry use product stage especially in the field of mold & die industry, cutting tools industry, electronics industry and automobile industry so on. A commercial scale production process utilizing SPS Method has been developed by applying an Advanced SPS machine systems, processing techniques and powder technology based on the triunity system concept. For the industrialization practically, it is essential to study on the technology integration. This is of great interest to the powder and powder metallurgy industry for both the new product developments and manufacturing applications. The ability of the advanced SPS process to apply a wide variety of materials in applications varying from structural materials to functional materials provides a versatility, high productivity and reproducibility with enormous potentiality for cost effectiveness and widespread use in a practical industrial product area. Power consumption of this new energy-saving sintering technique is about one third to one fifth compared to that of traditional hot press sintering. However, with the SPS system, it is critical to develop new manufacturing systems from the viewpoint of dynamically integrated processing, which develops both of software and hardware simultaneously by investigating sintering purpose, component cost, characteristics of raw powder materials and processes. In recent years, Five basic styles of production-type SPS machine systems were developed. Utilizing these SPS systems, various kinds of SPS applied industrial products are presently provided. As a typical high wear-resistant hard material, WC/Co system cemented carbides are now widely used in molds, press stamping dies, cutting tools and machine components for industrial applications. Disk-shaped WC/Co based cutting blades of 90mm to 200mm in diameter with thickness 0.35mm to 0.7mm were successfully fabricated by SPS. A binderless tungsten carbide material for Aspheric glass lens molding die were also developed by SPS. To improve the mechanical properties of monolithic hard materials into the surface with high hardness and inside with high toughness, a compositionally graded WC/Co and WC/Ni system FGMs were developed. The WC/Ni FGM having 40mm(width) x 30mm(length) x 5mm(thickness) with 3 layers graded composition of WC/Ni10wt%, WC/Ni15wt% and WC/Ni20wt% was homogeneously fabricated and ensured the weldability to normal steel materials without any cracks and delaminations. The FGMs were practically applied to a screw component of extruding machine and achieved more than 3 times longer life time at economical running cost. Firstly, in my talk, a brief historical review on progress of SPS technology is given and the applicable field is exemplified. Then, present developments and future prospects of Spark Plasma Sintering and Synthesis on research and industrialization activities in Japan will be introduced. The lecture is focused on industrialization of FGMs by SPS technology.

CB-12.1:IL02 Comparison of Microwave and Conventional Sintering of LHA Ceramics and Functionally Graded Alumina-LHA Ceramics

Zahra Negahdari*, Monika Willert-Porada, Chair of Materials Processing, Faculty of Engineering Science, University of Bayreuth, Bayreuth, Germany

Lanthanum hexaaluminate (LHA), LaAl11O18, is a coating material for fibre-matrix interface adjustment as well as an in-situ platelet reinforcement in ceramic composites. Fields of application are e.g., thermal barrier coatings and combustion catalysts. The low thermal conductivity of LHA combined with high structural reliability of alumina matrix ceramics attracted our attention to develop a new functionally graded layered LHA-Al2O3-composite (FGLHA), with a LHA and a porosity gradient along the thickness of a bulk oxide ceramic. LHA is formed by in-situ reaction sintering. The high sintering temperature required for completion of LHA formation in LHA-rich layers causes grain growth and a degradation of mechanical strength in alumina-rich layers. Microwave hybrid heating was investigated as a method to enhance the reaction rate without excessive grain growth. Comparison of conventionally and microwave assisted sintered homogenous composites with 2.8-80vol% LHA showed that utilization of microwave heating could enhance the solid-state reaction and densification in samples with more than 20vol% LHA. Enhanced microwave absorption in LHA rich layers assisted the sintering of a FGLHA at lower temperatures, enabling LHA formation without any abnormal grain growth in alumina rich layers.

CB-12.1:L04 Fabrication of Functionally Graded ZTA Ceramics Using a Novel Combination of Freeze Casting and Electrophoretic Deposition (EPD)

A.Preiss*, B. Su, University of Bristol, Department of Oral & Dental Science Lower Maudlin Street, Bristol, UK

Bone is a typical functionally graded material with hierarchical structures at multi-scales. A gradual increase in the pore distribution from the interior to the surface renders it with remarkable mechanical properties. It has been a long standing challenge as how to fabricate such bone-mimicking materials with controlled microstructures. Using the novel process of unidirectional freeze casting in combination with electrophoretic deposition (EPD), zirconia toughened alumina (ZTA) was investigated in this work to produce functionally graded ceramics with an open porous aligned structure on one side and a dense layer on the other side. Previous works showed that by varying the solid concentration and freezing velocity the ice crystal size and their morphology were adjustable. Furthermore, it has been identified that double side cooling render possible tailored ceramic specimen in terms of lamellae spacing. In the EPD process, an electrical field forced the charged particles in the slurry to move towards an electrode and formed a dense deposition. In order to achieve stable slurries, characterisations such as particle size, sedimentation rate, viscosity and zeta potential have been carried out firstly. An electric field was applied over the aqueous suspension followed by unidirectional freezing in a purposely designed double side cooling apparatus. When controlled cooling rate was applied from both sides of the slurry, the desired microstructures (lamellae spacing) have be produced over a thickness of several centimetres. By implementing a temperature gradient during freeze casting the structure and the composition gradually changed over the volume while under constant freezing conditions the spacing could be kept constant over the height. The macro- and microstructures were characterised using optical and scanning electron microscope (SEM) and X-ray microtomography (micro-CT). The results demonstrated that the lamellae channels of the sintered ceramics had a short axis up to 125µm and a long axis up to 1100µm at a height of 60mm. With this novel combination of freezing casting and EPD, tailored lamellae spacing was achievable.

CB-12.1:IL06 Functionally Graded Materials (FGM) and Spark Plasma Sintering (SPS)

M.P. Dariel*, Ben-Gurion University of the Negev, Beer-Sheva, Israel

The Functionally Graded Materials (FGM) concept was conceived in Japan in the mid-eighties of the last century, the development of the Spark Plasma Sintering (SPS) technology followed a few years later. The FGM concept relates to the design and processing of material parts and is applicable, in principle, to a variety manufacturing fields. SPS is essentially a novel technology that has gained great popularity over recent years providing convincing proofs of its advantages. Initially the FGM concept was linked to problems associated with the discontinuities present at the interfaces between different materials, e.g. ceramic and metallic. The realization of graded interfaces was meant to mitigate some of these problems. Stacked and sintered powder layers seemed an obvious solution path. It became soon apparent that the problem was much more complex and required modeling and or a trial and error approach. In this respect, the SPS technology is of great help by virtue of the very rapid return of experimental results. The review will consider the various applications of the combinations of FGM with SPS. These include nowadays bio-material, thermoelectric systems in addition to more conventional ceramic/ceramic and metal/ceramic combinations.

CB-12.1:IL07 Effects of Strain-graded Plastic Deformation on Mechanical Properties of Metals

Kiyotaka Matsuura*, Munekazu Ohno, Division of Materials Science and Engineering, Hokkaido University, Sapporo, Hokkaido, Japan

In a flow forming process of automobile wheels of Al-based alloys, plastic deformation of the rim part is performed by rollers from the periphery side, while the inner periphery is fixed on a steel mandrel and is slightly deformed. Therefore, the rim part has a strain-graded microstructure in the thickness direction. In this study, the effects of the strain-graded plastic deformation on mechanical properties of an Al-Si cast alloy have been investigated. The strain-graded plastic deformation in this study was done by hot rolling an Al alloy plate together with a steel plate. The two plates were joined at one end in the longitudinal direction and were rolled from the joined edge at 330 ^{o}C using a roller with a roll diameter of 200 mm and a rotation speed of 66 per minute. The chemical composition of the alloy was Al-7mass%Si-0.3mass%Mg-0.3mass%Fe. The rolled Al alloy plate had a strain-graded microstructure in the thickness direction.ing; the strain was the highest at the roller side surface and the lowest at the steel plate side surface. The rolling also brought about a Si particle size graded microstructure. The eutectic Si rods were broken by the rolling deformation and the Si particle size was the smallest at the roller side surface and the largest at the steel plate side surface. On the other hand, a normal rolling deformation of the Al alloy plate without the steel plate was also performed for comparison. The rolled sample having the strain-graded and Si particle size graded microstructure exhibited much more excellent bending strength and ductility compared with the normally rolled sample.

CB-12.1:L08 CMC with a Graded Lay-up Manufactured via LSI-process

Martin Frieß*, Christian Zuber, Bernhard Heidenreich, German Aerospace Center (DLR), Institute of Structures and Design, Stuttgart, Germany

Ceramic matrix composites (CMC) armed by long fibres are promising candidates for structural applications due to their damage tolerance even at very high temperatures. Since CMC based on SiC fibres are still very costly most cost-efficient CMC are based on carbon fibres. Among the processing routes for CMC most common for industrial applications is the liquid siliconization infiltration process (LSI) developed by DLR. In this three-step-process (CFRP manufacture, pyrolysis, siliconization) the fibre matrix bonding is determining the final microstructure, SiC content, mechanical properties and damage tolerance as well as oxidation and abrasion resistance. In general, higher SiC content enhances oxidation and abrasion resistance, however, lowers mechanical properties and damage tolerance significantly. For components applied in severe environments it is thus, desirable to have a SiC rich outer layer bearing a core being capable to carry high mechanical loads. Another possibility to obtain CMC with a graded lay-up concerning mechanical properties can be achieved by filament winding using a combination of selected winding angles, especially on tubes. In this paper several methods to manufacture CMC with a graded lay-up as well as properties and potential applications are presented.

CB-12.1:L09 **High Reliability Alumina-silicon Carbide Laminated Composites**

F. De Genua*, V.M. Sglavo, DIMTI, University of Trento, Trento, Italy

High mechanical reliability and surface damage insensitivity can be obtained by laminated structures able to develop, in processing, a specific residual stress profile with a maximum compression at a proper depth from the surface[1]. Following this approach, low-density laminates in the alumina/silicon carbide system were designed and fabricated by thermo-compressing tape cast layers, the obtained laminate being consolidated by pressureless sintering or Spark Plasma Sintering (SPS). Mechanical characterization was carried out by using the ring-on-ring loading configuration; fracture behaviour was analyzed both on as produced and on pre-indented samples and specific observations were performed to point out the stable growth of surface cracks. The reliability was evaluated in terms of Weibull modulus or minimum threshold strength. The mechanical performances were analyzed in terms of the consolidation process and correlated to the composition and architecture of the laminates.

[1] V.M. Sglavo, M. Paternoster, M. Bertoldi, "Tailored residual stresses in high reliability alumina-mullite ceramic laminates," J. Am. Ceram. Soc., 88 [10] 2826-2832 (2005)

CB-12.1:L10 **Control of Crystallographic Orientation in Alumina Laminate Using EPD in a Strong Magnetic Field**

Tohru S. Suzuki*, Tetsuo Uchikoshi, Yoshio Sakka, National Institute for Materials Science, Tsukuba, Ibaraki, Japan

Layered structure has been proposed as an alternative for the design of structural ceramics. The energy release mechanisms during the crack propagation can improve the crack growth resistance in the laminar ceramics. The residual stress generated in each layer has an influence on the crack deflection and crack bifurcation; hence the control of the residual stress is important. Our concept is that the crystalline axis depending on the thermal expansion coefficients aligns for controlling the residual stress in the monolithic ceramics. Alumina has the trigonal crystal structure with the each axis depending on the thermal expansion coefficients. Consequently, it is expected that the alumina layers contain the residual stress if the laminate with different crystalline-oriented layers can be produced. We reported that the development of the orientation in alumina controlled by electrophoretic deposition (EPD) in a strong magnetic. Hence, in this study we attempt to produce alumina/alumina laminar composites with different crystalline-oriented layers for controlling the residual stress using the difference of the thermal expansion in each layer and to study the crack penetration/deflection and the fracture behavior in the laminar alumina composites.

Session CB-12.2
Layered and Graded Thin and Thick Coatings

CB-12.2:IL01 **Multifunctional Nanostructured Films for Biomedical Applications**

D.V. Shtansky*, I.A. Bashkova, A.N. Sheveiko, E.A. Levashov, National University of Science and Technology "MISIS"; N.A. Gloushankova, Cancer Research Center, Moscow; A.S. Grigoryan, Central Research Dental Institute, Moscow, Russia

A new approach to design perspective multifunctional bioactive nanostructured films (MuBiNaFs) for metallic and polymer implants is described. MuBiNaFs were deposited by magnetron sputtering and ion implantation assisted magnetron sputtering of composite targets TiC0.5+X and (Ti,Ta)C+X {where X=CaO, TiO2, ZrO2, Si3N4, Ca3(PO4)2, and Ca10(PO4)6(OH)2}. The film morphology, grain size, texture, surface roughness, and phase composition were examined using a combination of various microanalytical techniques. The films were characterized in terms of their adhesion to various substrates, hardness, elastic modulus, elastic recovery, fatigue, wettability, surface charge, electrochemical characteristics, friction and wear both in air and under physiological and biological solutions. The biocompatibility and bioactivity of the films were evaluated by both in vitro and in vivo experiments. The results obtained show that MuBiNaFs possess a combination of high hardness, adhesion and fatigue strength, reduced Young's modulus, low wear and friction, high corrosion resistance with high level of biocompatibility, bioactivity, and biostability that makes MuBiNaFs promising candidates as protective films on the surface of metallic and polymer implants.

CB-12.2:IL02 **Fabrication of Porous Intermetallic Thick Films by Metallic Powder-liquid Reaction**

T. Ohmi*, M. Iguchi, Hokkaido University, Sapporo, Hokkaido, Japan

We introduce the concept of functional microchannel lining. As an example, we describe the composition and structure of a Ni-Al intermetallic layer lining the inner wall of the microchannel produced by a powder-metallurgical process utilizing microscopic reactive infiltration and/or diffusion. The Ni-Al lining layer is a thick film consists of multiple sub-layers and has a peculiar porous structure, in which long and thin micropores had grown along the thickness direction of the film. In our experiment, a nickel-powder compact containing shaped aluminum wire was sintered at temperatures between the melting points of nickel and aluminum. Molten aluminum migrated into the surrounding nickel powder and reacted with nickel, and thus a microchannel and a Ni-Al intermetallic lining layer were produced. In this process, nickel powder composed the device body, and the aluminum wire gave the shape of the microchannel and act as the aluminum source for the lining layer. Metallographical examinations revealed that both aluminum concentration and voidage in the Ni-Al lining layer show a graded distribution along the thickness direction of the layer. Such a porous structure is appropriate for a catalyst support used for high-temperature reactions.

CB-12.2:IL03 **High-strength Reaction-sintered Silicon Carbide for Large-scale Mirrors**

Shoko Suyama*, Yoshiyasu Itoh, Power and Industrial Systems R&D Center, TOSHIBA Corporation, Yokohama, Japan

The reaction-sintered silicon carbide (New-Technology Silicon Carbide: NTSIC) of 1000MPa class bending strength has been newly developed. We confirmed that the high-strength of NTSIC was determined by the size of residual silicon and the bending strength increased with decreasing the size of residual silicon. The bending strength over 1000MPa could be achieved to control the size of residual silicon under 100nm. The strengthening mechanism of NTSIC due to piled-up dislocation could be supposed on the investigation of physical fracture model. Also, we confirmed that the annealing heat treatment is effective to improve the bending strength of NTSIC by inducing the compressive residual stress at the surface oxide layer. On the other hand, the newly developed NTSIC showed the good rigidity, high thermal conductivity and high density as same as the conventional sintered silicon carbide. The newly developed NTSIC is one of the most attractive materials for large-scale ceramics structure, because of low processing temperature, good shape capability and low-cost processing and high purity. From the viewpoint of described above, we have been fabricated some lightweight space mirrors, such as NTSIC mirror substrate of 650mm in diameter.

CB-12.2:IL04 **Development of Functionally Graded Coating Based Plasma Facing Materials for Fusion Reactor**

Chang-Chun Ge[1, 2], Shuang-Quan Guo[2], Yun-Biao Feng[2], Zhang-Jian Zhou[1], Wei-Liang LiuU[2, 3], Juan Du[4]*, [1]Institute of Nuclear Materials, University of Science and Technology Beijing (USTB), Beijing, P.R. China; [2]School of Materials Science & Engineering, Southwest Jiaotong University, Chengdu, P.R. China; [3]Jingdezhen Ceramic Institute, Jingdezhen, P.R. China; [4]Max-Planck-Institute for Plasma Physics, München, Germany

Different coating technologies, such as plasma spray (PS), physical vapor deposition (PVD) and chemical vapor deposition (CVD), were applied for the fabrication of plasma facing materials (PFM) in fusion reactor, which can fabricate the PFM and join it to heat sink materials simultaneously. In the Institute of Nuclear Materials, University of Science and Technology Beijing (USTB), the concept of functionally graded materials (FGMs) was adopted to fabricate coatings for effectively alleviating the thermal stress generated between coatings and the substrate materials under high heat flux loading (5~30MW/m2). In the last several years, functionally graded coatings, including B4C/Cu, W/Cu and Mo/Cu systems were successfully fabricated by PS. The microstructure, mechanical properties and high heat flux properties of the FGM coatings were discussed in this paper. The results indicated that the porosity of the coatings fabricated by vacuum plasma spray (VPS) examined by image analysis is about 3%~5%, and the thickness of the coatings is about 1~2mm. The PS technology is an effective way to fabricate the functionally graded coatings, and the functionally graded coatings could effectively alleviate the thermal stress compared to the non-FGM coatings.

CB-12.2:IL05 Electrodeposition of Functional Molecules for Biomaterials

T. Hanawa*, K. Oya, K. Kurashima, Y. Tsutsumi, H. Doi, N. Nomura, Institute of Bioamaterials and Bioengineering, Tokyo Medical and Dental University, Tokyo, Japan

Recently, biofunctions are required for metals for biomedical use. Poly(ethylene glycol), PEG, is a biofuctional molecule on which adsorption of proteins is inhibited. Therefore, immobilization of PEG to metal surface is an important event to bio-functionalize the metal surface. PEG modified both terminals or one terminal with amine bases was immobilized onto titanium (Ti) surface using electrodeposition. PEG modified at both terminals or one terminal with amine bases was immobilized onto Ti surface. PEG-immobilized Ti with electrodeposition inhibited the adsorption of protein, adhesion of cells, adhesion of platelet, and formation of biofilm on Ti. On the other hand, the effect of a cell-adhesive peptide containing Arg-Gly-Asp (RGD) immobilized through PEG zwitterion with -NH2 and -COOH on Ti on calcification by osteogenic MC3T3-E1 cells was accelerated. Therefore, the hard tissue compatibility of Ti is improved by immobilizing RGD through functional molecules which have a long molecular chain. This immobilization technique is effective to control protein adsorption, cell adhesion, platelet adhesion, formation of biofilm, bone formation, and soft tissue adhesion.

CB-12.2:L06 Multifunctional Ti Oxide-based Films for Biomedical Applications

A.C. Alves[1], P. Ponthiaux[2], L.A. Rocha[1, 3]*, [1]CT2M, Univ. of Minho, Portugal; [2]LGPM - Ecole Centrale Paris, France; [3]DEM - Univ. of Minho, Portugal

The characteristics of the surfaces of implants may be considered as critical for the long-term success of the system. For instances, all the events involved in the bone growth around an implant (protein adsorption, cell adhesion and proliferation, etc.), are dependent on the composition, structure, and topography of the top surface layers of the material at a multi-scale level. At the same time, surface mechanical properties (essentially tribological and fatigue characteristics) together with chemical/electrochemical degradation resistance are also key aspects to be considered. The main aim of this work was to use anodic treatment for the surface modification of pure titanium. The influence of the processing variables on the evolution of the thickness, structure, composition and topography of the oxide-based films was investigated. Ca and P were introduced in the films in a one-step process and in different ratios, depending on the treatment conditions. Substantial different surface topography (at the nano- and micro scale) could be obtained. Tribocorrosion tests revealed that the degradation of the surface is strongly dependent on the composition and structure of the films. Preliminary biocompatibility tests suggests an adequate cell adhesion and proliferation.

Session CB-12.3
Modeling of Materials and Processes

CB-12.3:IL01 Processing of Ceramic Coatings and Multilayered Ceramics

Rajendra Bordia*, University of Washington, Seattle, WA, USA; Olivier Guillon, Technische Universität Darmstadt, Darmstadt, Germany; Christophe Martin, CNRS/ Grenoble-INP, Laboratoire SIMAP, Saint Martin d'Heres cedex, France

The continuum formulation for constrained and stress assisted sintering provides a versatile approach that can be used for a range of interesting and relevant problems. The basic framework of this approach and a theoretically sound, isotropic formulation will be presented to set the background for this talk. Results from the use of this approach to investigate crack growth in constrained sintered films will be presented and shown to be in good agreement with experimental results on both glass and crystalline films. A short summary on the use of this approach to predict and explain gross shape distortion (warping) in multilayered sintering systems will also be presented. However, this isotropic formulation has not been able to adequately predict the densification behavior of constrained ceramic films. Detailed and quantitative microstructural examination has revealed that due to the strain anisotropy, the microstructure of constrained films becomes anisotropic. An interesting observation is that in constrained films, the pores preferentially orient perpendicular to the substrate as sintering proceeds. Numerical simulations have also confirmed these observations. Finally, a transversely isotropic formulation for sinter-forging and constrained sintering will be presented. Thermodynamic bounds on the transversely isotropic constitutive parameters will also be addressed.

CB-12.3:IL03 Dual Scale Failure Modeling of Composite Structures for a Fusion Reactor

Jeong-Ha You, Max-Planck-Institute of Plasma Physics, Garching, Germany

The structural reliability of a composite component reinforced with a fibrous metal matrix composite is essentially affected by the micro/meso-scale failures. The micro-scale failures such as fiber fracture or matrix damage are directly governed by the internal stress states such as mismatch thermal stress. A proper computational method is needed to obtain micro/meso-scale data of stress and strain under thermo-mechanical loads. In this work an integrated computational scheme of micro/meso-scale failure analysis is presented for a composite component. Micromechanics-based dual-scale FEM was developed using a composite laminate element. The considered composite component was the plasma-facing components of a fusion reactor consisting of a tungsten block and a composite cooling tube. The micro/meso-scale stress and strain data were estimated for a heat flux pulse. Ductile damage of the matrix was estimated by means of a damage indicator. The risk of meso-scale plastic instability was estimated by comparing the homogenized meso-scale lamina stresses with the computed shakedown boundaries as a failure criterion.

CB-12.3:L04 Magnetoelectric Characterization of Compositionally Graded Magnetostrictive-piezoelectric Layered Structures

V. Petrov*, Novgorod State University, Veliky Novgorod, Russia; G. Srinivasan, S.K. Mandal, Oakland University, Rochester, MI, USA

The key goal of this study is to investigate the magnetoelectric (ME) coupling in functionally graded magnetostrictive-piezoelectric layered structures. A linear grading of the piezomagnetic coefficient in the magnetic layers and piezoelectric coefficient in the piezoelectric layers are assumed. The varying piezomagnetic and piezoelectric properties cause flexural deformations that result in inhomogeneous ME effect. Theoretical modeling is based on solutions of equation for flexural deformations, law of elasticity, and constitutive law. The ME coupling due to bending deformations have been measured for layered structures of nickel zinc ferrite with the grading axis perpendicular to the sample plane and lead zirconate titanate. It is well-known that in Zn-substituted nickel ferrite, the piezomagnetic coefficient varies linearly with increasing Zn concentration x for $x < 0.3$. Using the opposite poling directions of piezoelectric layers is shown to enable eliminating the standard ME effect stipulated by longitudinal deformations so that one can obtain only ME output due to grading effect. The ME voltage coefficient was found to be proportional to the piezomagnetic coefficient gradient. The modeling results match well with the experimental data.

CB-12.3:L05 Computation of Mixed-mode Stress Intensity Factors

A. Shaghaghi Moghaddam*, R. Ghajar, Mechanical Engineering Dept., University of KNTU, Tehran, Iran; M. Alfano, Mechanical Engineering Dept., University of Calabria, Rende (CS), Italy

The focus of the present work is to extract mixed mode stress intensity factors along 3-D curved crack fronts in Functionally Graded Materials (FGMs). The interaction energy integral is employed to this purpose because of its general applicability to problems where the mode of fracture is mixed. In the interaction energy integral method, auxiliary fields are introduced and superposed on actual fields. The actual fields are the results of finite element computation carried out by a finite element software whereas plane strain asymptotic Williams' solution for homogenous materials is chosen as auxiliary fields. Through a suitable definition of the auxiliary fields, the interaction energy integral can be related to the mixed-mode stress intensity factors. The contour interaction energy integral is herein expressed in the equivalent domain form that is well suited for numerical calculation. In FGMs both material nonhomogeneity and crack front curvature contributes to interaction integral formulation. In particular, material gradation leads to path dependency of J-integral, and imposing the auxiliary fields along curved crack front results in the lack of equilibrium and compatibility in auxiliary stress and strain fields, respectively. Hence, in order to capture the effects of material nonhomogeneity and crack front curvature, additional terms need to be incorporated in the interaction energy integral formulation. It is worth noting that in previous works related to analysis of fracture in 3D FGMs, the influence of crack front curvature in interaction integral formulation was neglected. Moreover, for graded materials, the mode of fracture is inherently mixed. Material gradation doesn't influence the square root singularity in the vicinity of crack tip but it does affect the mixed-mode stress intensity factors. Therefore, in the paper the influence of crack front curvature and material nonhomogeneity on mixed-mode stress intensity factors for 3-D planar curved crack in FGMs is explored. To this purpose, an isoparametric graded finite element is implemented in the finite element software ABAQUS exploiting the user element (UEL) capabilities. By using this improved interaction integral formulation augmented in Abaqus, the mixed mode stress intensity factors are calculated for penny-shaped cracks embedded in FGM cylinders.

Poster Presentations

CB-12:P01 Defect Crystal Structure of Low Temperature Modifications of Li2MO3 (M=Ti, Sn) and Related Hydroxides

N.V. Tarakina, T.A. Denisova*, Y.V. Baklanova, L.G. Maksimova, Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia; R.B. Neder, Kristallographie und Strukturphysik, Universität Erlangen, Erlangen, Germany

The Li2MO3 (M = Sn, Ti) compounds are promising materials for solid breeders in fusion reactors and are widely used as precursors, however their reactivity strongly depends on the synthesis condition. It has been shown that the low-temperature (LT) modification is more chemically active, which can be attributed to its structural features. The main reflections in X-ray powder data of LT - Li2MO3 can be indexed in a monoclinic unit cell, sp. gr. C2/c, resulting in a distorted cubic closed-packed network of oxygen atoms with octahedral cavities occupied by Li+ and M4+ ions. Lines of diffuse scattering in the electron diffraction patterns and Warren falls in powder patterns indicate random stacking of LiM2O6 slabs along c*. Displacements of LiM2O6 slabs lead to the formation of three structural modifications with short-range order in sp.gr. C2/c, C2/m or P3121. Crystal structure with random stacking of three possible space groups has been simulated and refined using the DISCUS software package. It has been shown that the probability of short-range order in sp.gr. C2/m is dominant for both cases. Based on obtained results crystal structure of new layered hydroxides MO(OH)2 has been solved and refined.

CB-12:P02 Layered Alumina Ceramics with Porosity Steps

E. Gregorová*, M. Chmelícková, Z. Zivcová, W. Pabst, ICT Prague, Prague, Czech Republic

This work deals with the preparation and characterization of macroporous alumina ceramics and with the preparation of layered laminates with porosity steps in the range 20-50%. Layered structures are built up by sequential casting of ceramic suspensions containing corn starch (median size approx. 14 microns), using both starch consolidation casting (SCC) and traditional slip casting (TSC). In both techniques starch acts as a pore-former, which is eliminated during firing. The influence of the alumina concentration and starch content in the suspension on the porosity, pore size and pore connectivity in the individual layers is studied. Differential shrinkage of the layers in the case of SCC, caused by the different starch content, may be avoided by controlling the alumina content. Open porosity and pore throat size are determined by mercury porosimetry, total porosity and pore cavity size via microscopic image analysis. Problems of image analysis are discussed for the case of highly porous ceramics, and the determined integral porosity values are compared to those measured via the Archimedes method.

CB-12:P03 Relationship Between Microstructure and Hardness of ZrN/TiN Multi-Layers with Various Bilayer Thickness

Y. Aoi*, S. Furuhata, Ryukoku University, Seta, Otsu, Japan; H. Nakano, Toyohasi University of Technology, Toyohasi, Japan

Multi-layers synthesized by alternately depositing two materials on the nanoscale have been shown to exhibit enhanced mechanical properties of the materials. In this study, we synthesized ZrN/TiN multi-layers by ion beam sputtering. The bilayer thicknss was varied from 5 to 30 nm and the total thickness was 450 nm. Microstructure and mechanical properties of the ZrN/TiN multi-layers were characterized by transmission electron microscope (TEM), X-ray diffraction (XRD) and nano-indentor. The hardness reached to the maximum value, when the bilayer thickness was 22 nm. X-ray diffraction measurements indicate that ZrN/TiN multi-layeres were preferentially oriented to the [111] direction. When bilayer thickness was larger than 15 nm, two distict peaks of ZrN (111) and TiN (111) were observed. However, when the bilayer thickness was less than 10 nm, one diffraction peak which located between the diffraction peaks of ZrN (111) and TiN (111) was observed. TEM observation of the multi-layeres with bilayer thickness 20 nm showed the existence of strain fields and dislocations at the interfaces, although those decreased when reducing the bilayer thickness. It is considered that the hardness enhancement caused by strain fields associated with the interfaces between ZrN and TiN layers.

CB-12:P04 Atomic and Electronic Structure of Zinc and Copper Pyrovanadates with Negative Thermal Expansion

T. Krasnenko*, N. Medvedeva, V. Bamburov, Inst. of Solid State Chem., Urals Div. RAS, Ekaterinburg, Russia

Zinc and copper pyrovanadates are promising materials for micro- and optoelectronics due to their negative coefficient of volume thermal expansion (NTE). Besides solid solutions on the base of these compounds can be used to obtain graded materials with variable thermal coefficient. Thermal deformation of both Zn2V2O7 and Cu2V2O7 structures was studied. According to the structure NTE data of these substances is provided by zigzag shape of zinc (copper) columns alongside with stable distances between layers. With the help of the first principle method within the limits of electronic density functional a theoretical examination of changes of structural and electronic characteristics depending on temperature for α-Zn2V2O7 and α-Cu2V2O7 was carried out. According to the electronic structure obtained, a-Zn2V2O7 is a semiconductor. The conduction band is determined by vanadium states with small addition of unbound 2?-oxygen states. It is shown the main part of Cu3d states to be positioned in the low energetic region for α-Cu2V2O7. The bottom valence band is formed mainly by 2p oxygen states. The Fermi level falls on the peak of density of states. That points to probable essential role of magnetism. A direct correlation between enthalpy of formation and volume changes was ascertained.

Symposium CC

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF CERAMICS

Oral Presentations

Session CC-1
Corrosion

CC-1:IL02 Interaction Between Corrosion and Wear of Silicon Carbide

K.G. Nickel*, V. Presser, C. Berthold, University Tuebingen, Applied Mineralogy, Tuebingen, Germany

Starting from a review of the corrosion mechanisms and kinetics of silicon carbide under well defined steady state conditions (temperature, atmosphere etc) we discuss the tribochemical attack as a special case, which is characterised by pressure and temperature fluctuations and structural changes to the material. We will emphasize the case of water lubricated wear conditions and the need for modern microscopic analytical methods. The modelling of local physical conditions is constrained by both energy input considerations such as asperity collision and friction and information from phase transformation and chemical changes. It is shown that the structural changes - nanofication, amorphization, crack formation - control the real local environment and allow chemical interaction such as hydrothermal oxidation reactions, which in turn alter the wear process with time. The needs and chances for improved tribochemical wear experiments and models will be outlined.

CC-1:IL03 Stability of Oxides in High Temperature Water Vapor

Elizabeth J. Opila, NASA Glenn Research Center, Cleveland, OH, USA

Both non-oxide ceramics and metal alloys used in high temperature oxidizing environments rely on the formation of protective oxide scales for long term application. Many high temperature environments, such as combustion environments, contain large amounts of water vapor in addition to oxygen. Therefore the stability of the protective oxides Cr2O3, SiO2, and Al2O3 in high temperature water vapor is essential for long application lifetimes. Cr2O3, SiO2, and Al2O3 all form gaseous hydroxides which can result in rapid degradation of the oxide or underlying material. Thermodynamic data for formation of these gaseous hydroxides as well as kinetic models for volatilization are required for accurate prediction of component lifetime. In this presentation, experimental techniques for identifying gaseous hydroxides and determining thermodynamic data for hydroxide formation are reviewed. In addition, kinetic models for oxidation and volatilization in high temperature water vapor are presented for systems forming Cr2O3, SiO2, and Al2O3.

CC-1:L04 Influence of Hydrofluoric Acid Concentration and pH on Corrosion of Porous Multi-oxide Engineering Ceramics

Marju Mannila, Lappeenranta University of Technology Antti Häkkinen, Lappeenranta University of Technology, Lappeenranta, Finland

The object of the research was to compare the corrosion resistance of three types of multi-oxide technical ceramics in hydrofluoric acid containing aqueous media according to a full factorial experimental plan with pH and fluoride ion concentration as variables. The samples were a silicon carbide doped aluminium silicate material, and two membrane coated aluminium silicates with one containing a membrane on both sides of the ceramic plate. The cores contained more additives on alumina, while the membrane layers were of higher grade aluminium oxide. The samples were shaken in containers for up to two weeks, and their weight losses and remaining hardness were measured. Daily samples withdrawn from the liquid phase were analyzed for dissolved components, redox potential and fluoride content. Maximum recorded weight losses were in the range of 15.25 % with the double membrane material losing the least mass. Similar behaviour was recorded for the total amount of dissolved components where two-week sums added up to 40 mg/gceramic. The materials underwent large drops in hardness with remaining hardness values recorded to be less than 5 HV3 in the worst case for each of the materials. Differences within materials were noticeable and seemed to vary more with respect to fluoride concentration than pH.

CC-1:L05 Design of Nano- and Meso-structured Sol-gel Coatings

Sophie de Monredon-Senani*, Elisa Campazzi, EADS Innovation Works, Metallic Technologies and Surface Treatment Engineering, Suresnes, France; Clément Sanchez, François Ribot, Lionel Nicole, Julie Monget, Laboratoire Chimie de la matière condensée de Paris, UMR CNRS 7574-UPMC, Collège de France, Paris Cedex, France

The necessity of being compliant with European rules and with the new assembly technologies is now more than ever an important driving force to replace existing aeronautical protection schemes. In this context, our aim is to develop an innovative design of multifunctional sol-gel coating, including different functionalities in the meso- or microporosity, opportunely filled, for corrosion protection of light aeronautical alloys. In a first step, our approach is to elaborate a two layers protection scheme: 1) near the metal including corrosion inhibitors in the mesoporosity tuned by EISA process which is based on the organisation, during the coating formation, of self-assembled organic templates such as surfactants. 2) a dense and multifunctional coating designed at the nanoscale by the NanoBuilding Block approach: the assembly of well-defined starting units allows a better control for organic-inorganic interfaces and for the nanostructure of the coating than conventional sol-gel pathways. The sol-gel chemistry is compliant with thermal treatment applicable to aeronautical substrates and environmental concerns. Moreover, different functionalities such as coating mechanical reinforcement, colour. could be obtained by the introduction of additives into the hybrid material.

CC-1:L06 Electrochemical Corrosion of Silicon Carbide Ceramics in Aqueous Solutions

M. Herrmann[1]*, U. Sydow[2], K. Sempf[1], M. Schneider[1], H.J. Kleebe[3], A. Michaelis[2], [1]Fraunhofer Institute for Ceramic Technologies and Systems, Dresden, Dresden, Germany; [2]TU Dresden, Institute of Materials Science, Dresden, Germany; [3]Technische Universität Darmstadt, Institute for Applied Geosciences, Darmstadt, Germany

SiC- ceramics are electrically conducting. The conductivity strongly depends on kind and content of sintering additives and the sintering conditions. In LPSSiC materials the solution precipitation mechanism results in the formation of core-rim structures, which can be shown by special FESEM techniques and which will have different electrical properties. Recent investigations have shown that electrochemical corrosion processes can have a strong influence on the stability of SiC ceramics e. g. in sealings. Therefore, the electrochemical stability of different SSiC and LPSSiC ceramics were investigated in acids, basis and neutral solutions . The Investigations showed a strong dependence of the amount and distribution of the formed surface layers on the pH of the solution and the kind of ceramics. The microstructural analysis of the corroded samples showed strong local differences in the stability, which can be correlated with the starting microstructure. For example for LPS-SiC materials in basic solutions a clear preferential chemical attack of the rims of the SiC grains was observed.

CC-1:IL08 Tribological Performance of Polymer Coatings for Aggressive Sliding Conditions

Andreas A. Polycarpou*, Emerson Escobar Nunez, Seung Min Yeo, University of Illinois at Urbana-Champaign, Urbana, IL, USA

In many engineering applications, such as air-conditioning compressors, the need for protective coatings is necessary to protect contacting and sliding surfaces. Traditional hardening techniques and advanced bulk material replacement can not sufficiently protect the surfaces, especially when operating under extreme conditions (which are necessitated either from needed performance improvements or the need to operate under oil-less conditions). Moreover, traditional hard and super-hard coatings may not offer the required surface protection in applications such as compressors due to cost, surface preparation and inability for long-term scuffing protection. A recent alternative solution is the use of polymeric-based coatings, which can readily be coated to numerous engineering materials and offer the needed surface protection. Such coatings include polytetrafluoroethylene (PTFE) and polyetheretherketone (PEEK) based coatings with additives such as ceramics and molybdenum disulfide. In this lecture, tribological results under aggressive compressor conditions will be presented comparing several polymeric and hard coatings under oil-less conditions. Results with a newly developed polymeric-based coating, aromatic thermosetting copolyester (ATSP) with PTFE will also be presented.

CC-1:IL09 Changes in Surface Properties of Alumina Toughened Zirconia (ATZ) by Hydrothermal Aging and Wear

J. Schneider*, Ch. Kaps, Bauhaus University Weimar, Department of Building and Material Chemistry, Weimar, Germany; S. Begand, Th. Oberbach, Mathys Orthopaedie GmbH, Moersdorf, Germany

ATZ ceramic is a composite ceramic for the use in total hip joint prosthesis. It consists of 80 wt. % 3Y TZP (zirconia) and 20 wt. % Al2O3 (alumina). In use, the material is subjected to low temperature degradation (LTD) as well as tribological stress. The aging kinetics of ATZ and 3Y-TZP were simulated at body temperature up to 50 years. The wear tests were carried out on modified ball-on-disc samples. Both, the aged and the tribologically stressed samples were analysed by gracing incidence x-ray diffraction and Knoop microhardness measurements. Both methods allow depth resolved investigation of the phase composition and the mechanical strength respectively. The surface morphology is observed by AFM and SEM. The simulation of aging kinetics shows, that ATZ has a considerable higher aging resistance than 3Y-TZP over 50 years in water vapour. Microhardness measurements indicate a reinforcement effect of the material at small amounts of monoclinic phase. The tribological stress also leads to a surface strengthening in a thin surface layer. AFM observations after wear test show a smeared surface with very low roughness.

CC-1:L10 Corrosion of Single Crystal Cordierite by Model Diesel Particulate Ashes

Nicolas Maier, Klaus G. Nickel, University Tuebingen, Applied Mineralogy, Germany; Christine Engel, Andreas Mattern, Robert-Bosch AG, Stuttgart, Germany

Cordierite Mg2Al4Si5O18 is a candidate material for diesel particulate filters (DPF). Two simplified model ashes, considered to be realistic for use under ‘worst case’ conditions, have been applied to single crystals at temperatures up to 1050°C. Single crystals were examined in order to investigate the orientation dependence of attack due to the strongly anisotropic nature of the Cordierite crystal lattice. A mixture of sodium carbonate and silica was used to study the attack of an alkali-rich ash composition. It attacked the Cordierite by dissolving it slowly. No anisotropy in the corrosion was observed. In contrast a mixture of Ca, Mg and Zn orthophosphates showed excessive melt formation , which caused fast dissolution of the substrate with melt saturation within minutes. Anisotropy of the dissolution process could not be detected. The initial kinetics is dominated by saturation effects, which slow down corrosion. The saturated melt attacks Cordierite by reaction processes leading to the formation of new crystalline phases, which can cause the extension of faults.

CC-1:L12 Study of Corrosion Behavior of Conventional and Nanostructured WC-Co HVOF Sprayed Coats

Sh. Khameneh Asl[1]*, M.R. Saghi Beyragh[2], M.G. Kakroudi[1], [1]Department of Materials Engineering, Faculty of Mechanical Engineering, University of Tabriz, Tabriz, Iran; [2]Faculty of Materials Engineering, Sahand University of Technology, Tabriz, Iran

Interest in nanomaterials has increased in recent years. This is due to the potential of size reduction to nanometric scale, which improve properties of materials such as hardness, toughness, wear, and corrosion resistance. The current study is focused on WC-Co cermet coats, materials that are extensively used in applications requiring wear resistance. In this work, WC-17Co powder was thermally sprayed onto mild steel using High Velocity Oxy Fuel (HVOF) spray technique. The nanostructured specimen was produced from sprayed samples by heat-treating at 1100°C in a vacuum chamber. Their structures were studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Polarization and electrochemical impedance spectroscopy (EIS) tests were performed on both types of coated samples in 3% NaCl solution. The amorphous phase in WC-17Co coating was transformed to crystalline phases by heat treatment at high temperatures. Heat treatment of these coatings at high temperature also resulted in partially dissolution of WC particles and formation of new crystalline phases. Generation of these phases produced the nanostructured coating with better mechanical properties. Comparative electro chemical test results showed that, the heat treatment could improve corrosion resistance of the nanostructured WC-17Co coat than the as sprayed coats.

Session CC-2
Friction and Wear

CC-2:IL01 Wear Mechanisms of Nanocrystalline Ceramic/Metal Composites

F. Gaertner*, H. Kreye, T. Klassen, Helmut Schmidt University, Hamburg, Germany

As described by the Hall - Petch relation, the hardness of ceramic / metal composites can be increased by finer microstructures, resulting in better wear resistance. For designing application properties, the influence of reduced toughness under increased hardness must be considered. One possible solution is offered by nanocrystalline composites, which at higher hardness still show reasonable toughness. The contribution presents experimental results of wear tests investigated with microcrystalline and nanocrystalline composite coating and addresses different wear mechanisms. Due to their finer and more homogeneous microstructures, nanocrystalline composite coatings show significantly higher hardness and toughness and mechanically behave like a homogeneous material, resulting in continuous wear grooves. Under high stress, nanocrystalline coatings have superior wear resistance by a factor of 2, as compared to microcrystalline coatings, and are more reliable due to higher fracture toughness. Under low stress, the nanocrystalline coatings show a slightly higher wear than microcrystalline ones, however, with more homogeneous material loss, lower friction coefficient, and smoother worn surface, which may be more important for applications than the actual loss of material.

CC-2:IL02 Simulation of Atomic-scale Wear of Graphene

Naruo Sasaki*, Seikei University, Musashino, Tokyo, JAPAN

The atomic-scale wear, the formation process of the graphene during the lateral line scan process of the nanoscale tip on the multi-layered graphene substrate is studied by using molecular relaxation method. The nanotip is scanned in line forward (along [1230] direction) and backward under the constant-height mode. Analysis of the effect of the tip height on the relative motion of the nanotip, the 1st graphene layer, and the 2nd graphene layer, reveals the transition from the nanotip state to the graphene tip state. During the nanotip state the mean lateral force rapidly increases as the mean loading force increases. Here the friction between the tip and the surface occurs. However, during the graphene tip state, takes nearly the constant value independent of . Here the internal friction among the 1st, the 2nd and the 3rd graphene layers occurs. The marked scan directional dependence and the increase of near the graphene edge appears. The irreversible shift of the graphene layer after all the scan processes can explain the mechanism of the elementary process of the atomic-scale wear. Next the nanoscale peeling of the graphene sheet is studied. The force-distance curve reflects the transition of the graphene shape from the surface- to the line-contact.

CC-2:IL03 Wear in Nanofriction

Roland Bennewitz*, Philip Egberts, INM - Leibniz Institute for New Materials, Saarbrücken, Germany

Wear and friction are more closely connected than researchers employing friction force microscopy would like to believe. Surfaces exhibit atomic-scale wear scars after scratching with loads as low as a few nanonewtons[1]. The characteristics of the lateral force recorded while sliding repeatedly along a surface line may be dominated by debris structure[2]. Furthermore, several groups have now reported wear of the tip of the force microscope[3]. We will discuss the role of wear for friction measurements on the nanometer scale. We will also present multi-mode force microscopy experiments, in which wear produced by the indentation action of the tip in contact with the surface was subsequently investigated with high-resolution non-contact imaging of the resulting surface structure[4].

[1]E. Gnecco et al, Phys. Rev. Lett. 88 (2002) 215501; [2]A. Socoliuc et al, Phys. Rev. B 68 (2003) 115416; [3]R. Bennewitz and J.T. Dickinson, MRS Bulletin 333 (2008) 1174; [4]P. Egberts et al, Nanotechnology 20 (2009) 264005

CC-2:IL04 Advanced Evaluation Methods of Residual Stress in Bioceramics Wear Surfaces

Giuseppe Pezzotti*, Ceramic Physics Laboratory and Research Institute for Nanoscience, Kyoto Institute of Technology, Kyoto, Japan; The Center for Advanced Medical Engineering and Informatics, Osaka University, Osaka, Japan; Department of Orthopaedics, Orthopaedic Research Center, Loma Linda University, Loma Linda, CA, USA

Surface damages developed in vivo at the bearing surfaces of bioceramics couples result from repeated fretting contacts between hard surfaces in highly corrosive environment. Rationalizing wear processes relies on simulator experiments, with weight loss and surface roughness being the parameters assessing the quality of sliding couples. However, such outputs provide limited physical insight into the nature of surface damages. Recent spectroscopic studies of ceramic hip joints revealed significant effects from surface residual stress on bearing ceramic surfaces, hinting that lifetime predictions need a better understanding of contact stresses. Surface residual stresses progress with bearing history. They are yet the objects of debate and not even cautionary notes have been introduced into joint test standards. In this paper, we explore the suitability of confocal laser and electron probes in measuring the actual magnitude of surface residual stresses piled up in vivo on the surface of ceramic hip joints. The electron probe allows substantial improvement in spatial resolution, and gives the correct magnitude of wear stresses on the sample surface, thus rationalizing environmentally assisted wear effects in ceramic bearing surfaces.

CC-2:L05 In Situ Studies of Coatings Tribology

C. Muratore*, A.A. Voevodin, Air Force Research Laboratory, Thermal Sciences and Materials Branch, Wright-Patterson, OH, USA

Tribological studies of thin films often rely on post mortem forensics efforts, in which a wear test is conducted, and the structure and composition of the contact area is related to the wear test results. This routine presents difficulties in that the ambient conditions during the wear test are typically different than those in which ex situ characterization takes place. This is particularly true in the field of high temperature tribology, where new compounds form as the sample cools to a convenient temperature for handling and preparation for analysis. Several techniques to give real-time data on film characteristics, including wear track composition and crystal orientation, transfer film thickness, and coating wear depth and morphology have recently been used to characterize tribological coatings throughout a broad range of ambient conditions in our laboratory as well as in those of our collaborators. Example studies on wear track chemistry and transfer film thickness of TiCN films tested in different levels of ambient humidity, contact chemistry of MoS2 at elevated temperature, and the temperature-dependent surface chemistry and crystal orientation of adaptive high temperature coatings, such as VN-Ag which demonstrates low friction from 25-1000 °C, will be presented.

CC-2:L07 Effect of Polymorphic Zirconia Phases on the Mechanical and Wear Properties of Cr3C2-NiCr Cermets

Y.K. Tür, A. Özer*, C. Duran, Gebze Institute of Technology, GYTE Material Science and Engineering, Kocaeli, Turkey

Cr3C2-NiCr type cermets are used in cutting technology for their low sintering temperatures and relatively low densities. Their high corrosion resistance at high speeds and temperatures increases interest to these materials. In this study, the powder mixture of 75wt% Cr3C2-25wt% NiCr with a Ni-Cr ratio of 4/1 was produced as master composite at four different sintering temperatures for its microstructure, fracture toughness, transverse rupture strength and microhardness. ZrO2 in three different crystal structures (monoclinic, 3 mol % yttria stabilized tetragonal, 8 mol % yttria stabilized cubic) was added as dopant to study their effect on mechanical and wear properties Cr3C2-NiCr cermets. SEM and EDX analysis performed for identifying microstructures indicates that full densification occurs at 1300 °C and average grain size was measured as 4 µm. As the relative density increases, an increase in the micro-hardness, transverse rupture strength and fracture toughness of cermets was also observed. Pin on disc and scratch tests were performed to characterize the wear properties of the cermets.

CC-2:IL08 Nanoadhesion and Nanopeeling of Nanotube on Graphite

K. Miura*, M. Ishikawa, Department of Physics, Aichi University of Education, Kariya, Japan; N. Sasaki, Department of Materials and Life Science, Seikei University, Tokyo, Japan

Detachment and peeling experiments are expected to provide information on adhesion forces and adhesion energies of solid surfaces in contact. Such experiments are important in powder technology, in the formation of adhesive films and in understanding how cracks propagate in solid and how fracture occurs. Recently, nanoscale peeling has been studied by extending biological polymer chains such as proteins using atomic force microscopy to clarify the mechanical mechanism of unfolding of the polymer chain. Such experiments have attracted much attention worldwide as a new method of spectroscopy for the structural analysis of biological macromolecules. On the other hand, it has been more recently reported that carbon nanotube arrays with a curly entangled top show a macroscopic adhesive force of approximately 100 newtons per square centimeter, almost 10 times that of a gecko foot, and a shear adhesion force much stronger than the normal adhesion force. In this work, adhesion and peeling experiments on the MWCNT have been performed. We have experimentally obtained the vertical force-distance curve with the characteristic hysteresis loop, which exhibits multistable states between line contact and point contact of the MWCNT shape during the adhesion and peeling. The line and point contacts are clearly divided by the discrete jump that appeared in the vertical force-distance curve, which shows the nanoscale elastic property of the MWCNT. The adhesion and peeling behaviors of the MWCNT reveal hierarchical structures (or fractal structures) from the nanoscale intermittent to the mesoscale intermittent adhesion and peeling. The nanoscale intermittent behaviors depend strongly on the adhesion and peeling velocities, which reveals that the peeling occurs when a MWCNT goes over the potential barrier of the neighboring AB-stacking registry with the graphite substrate surface. On the other hand, the most probable pull-off forces depend weakly on the peeling velocities, which indicates that it is difficult to pull MWCNTs off the graphite substrate without a finite lifting force. Furthermore the mesoscale intermittent forces of the conformational transition indicate that the barrier position of the conformational transition is at least on the order of a MWCNT length.

CC-2:IL09 Nanoindentation and Small Scale Plasticity

E. Le Bourhis*, Université de Poitiers, Laboratoire de Physique des Matériaux, UMR 6630 CNRS, SP2MI, Futuroscope-Chasseneuil, France

Surface mechanics involves small length scales determined both by the contact characteristics and the material shape and nanostructure. It determines ceramics strength (flaw generation), wear and friction[1]. Routes are explored to treat and shape the surface and modify the elastic-plastic transition. In this field, the indentation technique has proved to be a powerful tool to test small volumes even at temperatures below the brittle-ductile transition, while transmission electron microscopy (TEM) allows for great insights into local plasticity[2]. In a first step, the behaviour of homogeneous bulks is reported and reviewed with emphasis on elastic-plastic transition, indentation plastic expansion, contact strains and stresses. In a second step, shaping or treating (with plasma and/or coatings) influence on the mechanical response is discussed in view of contact and nanostructure length scales. Elastic-plastic ratio can be tailored for wear applications, examples of nanostructured nitrides, sol-gel hybrid coatings being presented.

[1]E. Le Bourhis, D.J. Morris, M. Oyen, R. Schwaiger, T. Staedler. (Eds), MRS Proc. 1049 (2008); [2]E. Le Bourhis, Glass Mechanics and Technology (Wiley-VCH, Weinheim, 2007)

CC-2:IL10 Characterization of Wear Mechanisms of Silicon Carbide Materials

V. Presser*, K.G. Nickel, C. Berthold, Eberhard-Karls-Universität Tübingen, Institute for Geosciences, Applied Mineralogy, Germany

Wear processes are often only investigated by monitoring external physical loading parameters such as applied forces and resulting friction values and overall damage parameters such as volume or mass loss. We show the importance to carry out nanostructural characterization of worn surfaces to establish a basic understanding of the underlying processes during tribochemical deterioration. The case of water lubricated wear of silicon carbide is presented. Using state-of-the-art HR-TEM on foils prepared using focused-ion-beam (FIB) machining, we are able to discern between the chemical and the structural part of the deterioration mechanism. We show that only a combined effort of chemical analysis and phase identification using EDX, EELS, µ-XRD and Raman spectroscopy is capable of revealing a well constrained view of the physico-chemical conditions. A new perspective of these investigations is the feedback structural changes have on physical characteristics: we show, how a change in superficial thermal conductivity is measured and needs to be considered in future wear simulation models.

CC-2:L11 Study on the Development of Resource-saving High Performance Slurry - Polishing/CMP for HDD Glass Substrates, Using Slurry Mixed with Manganese Abrasives to Replace Ceria Abrasives-

T.K. Doi*, T. Yamazaki, S. Kurokawa, S. Isayama, Y. Umezaki, Y. Matsukawa, Dept. of Mechanical Engineering, Kyushu University, Fukuoka-shi, Japan; Y. Akagami, Akita Prefecturaru, R&D Center; Y. Yamaguchi, Mitsui Mining & Smelting Co., Ltd.; S. Kishii, Fujitsu Lab. Ltd., Japan

The polishing of glasses heavily consumes cerium oxide particles (CeO2), which is one of the rare metals today found difficult to obtain. There is a growing concern today that such circumstances will become a bottleneck problem for the future expansion of the industry. In this study, we selected manganese oxide particles expected to be effective for glass polishing, based on this mechanism. We have experimentally produced manganese oxide abrasives such as MnO, MnO2, Mn2O3 and Mn3O4, which were then burned in rotary kiln at 600 ~ 900 °C. These burned particles were dispersed in pure water to produce slurries. Using respective slurries, polishing characteristics of glass substrates were obtained, from which Mn2O3 abrasives burned at 850 °C was found the best in the polishing efficiency. It was also discovered that although removal rate tends to stop its increase when Mn2O3 abrasive concentration reaches 5wt%, the removal rate is as good as that of existing ceria oxide. Furthermore, roughness of the polished surfaces was below Ra0.8nm, which confirms Mn2O3 abrasives to be better by far than ceria. We are pleased of being able to propose here a new slurry designed for glass substrates, which contributes to the natural resources saving.

CC-2:L12 **Wear Behaviour of Diamond Coated Silicon Nitride Ceramics**

M. Herrmann, S. Sempf, A. Bales, M. Hoefer*, L. Schaefer, B. Blug, T. Hollstein, J. Koenig, Fraunhofer Allianz DIACER, Braunschweig, Germany

The coating of ceramics and hard metals with wear resistant CVD coatings (e. g. Ti(C,N)) is a well established technology for the improvement of the wear behaviour of cutting tools and other wear parts. CVD diamond coatings on Si3N4 ceramics have been developed in recent years. One challenge while researching these coatings is the lack of understanding of the adhesion. Therefore analytical methods for the investigation of the interface structure and adhesion were developed and tested at Si3N4/diamond composites. Strategies for the improvement of the adhesion and the wear behaviour of CVD coated ceramics could be developed based on the determined correlations between interface structure and wear behaviour.

CC-2:IL13 **Novel Approaches for Following Atomic Scale Wear**

W. Gregory Sawyer, Dept. of Mechanical and Aerospace Eng. University of Florida, Gainesville, FL, USA

When designing and constructing a tribometer, several benefits can be obtained by performing wear measurements in situ to the test environment. First, this simplifies the correlation between friction data and surface wear events. Additionally, the need to remove the sample from the test environment is eliminated and the risk of surface contamination greatly reduced. The paper reports on the design and operation of a reciprocating tribometer that resides under a scanning white-light interferometer. The tribometer has been used to quantify wear and rates of wear on a wide variety of solid lubricant films operating in air and inert environments. With the goal of in situ wear observation in mind, a tribometer has been constructed for use under a scanning white light interferometer (SWLI) microscope. SWLI microscopes can perform three dimensional surface profile measurements where the individual pixel heights are resolved with sub-nanometer precision. This affords the opportunity to accurately take wear measurements of inherently difficult surfaces such as thin films and coatings.

Poster Presentations

CC:P02 **Performance of Blended Cement Concrete Against Seawater Attack**

Hosam.El-Din H. Seleem[1], Alaa M. Rashad[1]*, Basil A. El-Sabbagh[2], [1]Building Materials Research and Quality Control Institute; [2]Raw Building Materials Technology and Processing Research Institute, Housing & Building National Research Center, HBRC, Cairo, Egypt

The current work reports the influence of synthetic seawater on some of the durability aspects of an ordinary concrete mixture (control) and six pozzolan-concrete mixtures. Three types of pozzolanic materials were employed; silica fume (SF), ground granulated blast furnace slag (GGBS) and metakaolin (MK). The pozzolanic materials were employed as an addition to cement in binary and ternary combinations. All mixtures were tested for strength deterioration ratio (SDR) after 3, 6, and 12 months of exposure to synthetic seawater, permeability, and chloride ion concentration (chloride ingress) at the surface layer and inside the specimens after 6 and 12 months of exposure. The mineralogical compositions of all mixtures were investigated by the X-ray Diffraction Technique (XRD) before and after exposure at two locations: inside and at the surface layer of the test specimens. It was found through this investigation that pozzolans increase the ability of concrete to withstand aggressive environment and prevent most of the deterioration signs. The pozzolanic materials serve also to increase the strength and to minimize the strength loss (SDR) upon exposure to seawater. Chloride ion concentration inside the specimens are pronouncedly reduced for pozzolan mixtures compared to the control specimens due to enhancing the microstructure and the ability of some pozzolans that contain a relatively high content of alumina to bind the chloride ions to the surface of specimens.

CC:P03 **Oxidation Resistance and Corrosion Resistance of Molybdenum-Chromium Nitride**

Masahiro Nagae*, Naoko Ise, Hideyuki Kuwahara, Research Institute for Applied Science, Sakyoku, Kyoto, Japan; Jun Takada, Graduate School of Natural Science and Technology, Okayama University, Japan

For Mo-Cr nitride layer prepared by NH3 gas nitriding of pure Mo subjected to Cr-diffusion treatment, the oxidation behavior in air and corrosion behavior in boiling sulfuric acid were investigated. The surface nitride layer consisted of Mo2N type solid solution of which Mo-Cr ratio was almost 1 : 1 on the surface. Although Mo2N layer obtained by nitriding pure Mo was oxidized at temperatures above 773 K, Mo-Cr nitride layer exhibited superior oxidation resistance up to 1073 K. The corrosion resistance of Mo-Cr nitride layer in boiling sulfuric acid was as excellent as that of Mo2N layer.

CC:P04 **Mechanical Properties of Silicon Nitride Using RUS & C-Sphere Methodology**

Mark Hadfield*[1], Wei Wang[1], Andrew Wereszczak[2], [1]School of Design, Engineering and Computing, Bournemouth University, Poole, UK; [2]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Silicon Nitride is a type of engineering ceramic which has been used in rolling element bearing and other rolling contact applications due to its good fatigue life, high temperature strength and tribological performance. In this paper, the mechanical properties of Hot Isostatically Pressed (HIPed) and Sintered and Reaction Bonded Silion Nitride (SRBSN) have been studied and realted to wear durability. The elastic modulus and poisson's ratio of three type of commerical grade HIPed silicon nitride, and ground SRBSN with three surface condidtions were measured using a Resonance Ultrasound Spectroscopy (RUS). The RUS measurement reveals the variation of elastic properties across different types of HIPed silicon nitride specimens. The surface strength of silicon nitride are studied using a C-Sphere specimen,and the results show that different commercial grade HIPed silicon nitride show varying surface strength. The surface conditions of ground SRBSN have an effect on the surface strength of the specimens. The RUS and C-Sphere techniques can potentially be used to sample the quality and consistency of silicon nitride rolling elements in terms of wear performance.

Symposium CD

CERAMIC JOINING

Oral Presentations

Session CD-1

Thermochemistry of Interface Formation and Mechanisms of Wetting and Adhesion

CD-1:IL01 **Contribution to the Theory of Ceramics/liquid Metal System Wettability. A Peculiarity of Contact Processes for Transition and Non=transition Metals**
Y. Naidich, Institute for Materials Science Problems of the National Ukrainian Academy of Sciences, Kiev, Ukraine

Theoretical concept on thermodynamic and atomic-electron levels for high temperature wettability processes in ceramic/metal systems is considered and developed. In non-equilibrium contact systems the wettability is conditioned by chemical interface reactions and nature and properties of a new phase formed at the liquid/solid boundary. Wetting mechanism is analyzed particularly for contact of liquid metals with ionic and ionocovalent substrates (first of all oxides). Transition metals (partly occupied d-electron bands) play a special important role in the process that provides high wettability. Strong cation-cation bonds of metallic character exist in lower oxides at electronic configuration 3dm ($m \leq 5$, better $m \leq 3$). The bonds are determined by overlapping of cation d-electron wave function (Ligand field theory). After interface oxidizing-reducing reaction occurred, bonds of metal-oxygen and metal-metal (neutral and positive ions) are formed. Special consideration is done for non-transition metal wetting and dewetting phenomena. Above mentioned is a ground to formulate thermodynamic and atomic-electronic conditions to reach good wetting in ceramic/liquid metal systems and use it in joining of ceramic materials, composite making etc.

CD-1:IL02 **Metal Ceramic Reactivity: Thermodynamics and Kinetics**
F. Hodaj, SIMAP-UMR CNRS 5266, Grenoble INP-UJF, Saint Martin d'Heres Cedex, France

Interfacial reactions between liquid metals and ceramics are of technological importance in many fields of materials engineering such as joining of ceramics by brazing alloys, manufacturing of metal/ceramic composites, casting of metals, etc. In non-reactive metal-ceramic systems non-wetting is usually observed. In these systems, wetting can be significantly improved by certain alloying elements which form continuous layers of compounds at the interface, by reaction with the ceramic substrate. Such reactions are used in practice to promote wetting, especially for joining of ceramics by brazing alloys. As this reactivity can affect the physical properties of the interface and especially the mechanical behaviour of the system, it is important to control the nature, morphology and microstructure of the reaction product. The purpose of this presentation is to focus on the fundamental issues of metal/ceramic interfacial reactions and to analyse the main thermodynamic and kinetic factors governing these reactions. In particular, some physicochemical aspects which can affect, or even control, the morphological evolution of the interfacial region will be discussed by using and analysing different examples of interactions between oxide or non-oxide ceramics and reactive liquid alloys.

CD-1:IL03 **Thermodynamic Evaluation of Interface Formation in Ceramic/Metal Systems. Boron Carbide/Metal Systems**
N. Frage[1]*, M. Aizenshtein[2], N. Froumin[1], M.P. Dariel[1], [1]Dept. of Material Engineering, Ben-Gurion University, Beer-Sheva, Israel; [2]NRC-Negev, Beer-Sheva, Israel

Ceramic-metal interfaces play a major role in determining the properties of ceramic-metal composites, in the interaction of crucibles with molten metals, and in the ceramic/metal joining technology. The possibility of predicting the formation and evolution of such interfaces is of cardinal importance, for an the improved design of such systems and for the optimization of these technologies. The presentation focuses on the thermodynamic analysis of interface formation in boron carbide/liquid metal systems. Although boron carbide has excellent mechanical properties, its chemical stability in contact with liquid metals is relatively low. Boron carbide exists over a wide composition range (B4C-B10C) and the activity of its components strongly depends on the carbide composition. The nature of the interaction between boron carbide and metals depends on the affinity of the liquid metal to boron and carbon. For a higher affinity of the liquid metal to boron than to carbon (the case of Ti, for instance), the interaction results in the formation of a boride phase and the precipitation of free carbon at the interface. If the metal has a high affinity to carbon (Si, for instance), the formation of a new carbide phase and shift of the boron carbide stoichiometry takes place at the interface.

CD-1:IL04 **Wetting of Ceramics by Molten Mg**
H. Fujii[1]*, S. Izutani[1], S. Kiguchi[2], K. Nogi[1], [1]Joining and Welding Research Institute, Osaka University, Osaka, Japan; [2]Kinki University, Higashi-Osaka, Japan

The wetting of several ceramics by molten Mg and the surface tension of molten Mg was measured between 973K and 1273K using an improved sessile drop method, because magnesium is one of the best candidates for the matrix of a composite material. For the MgO samples, poly-crystal MgO plates, and (100) and (111) single crystal MgO plates, for the Al_2O_3 samples, poly-crystal Al_2O_3 plates and R(0112), and C(0001) single crystal Al_2O_3 plates were used. In this method, molten magnesium was set around the sample droplet to prevent oxidation of the magnesium droplet. As a result, the wettability and surface tension were measured without any oxidation of the Mg droplet. A significant volume loss of the droplet was observed over 1073K due to the high vapor pressure, and the contact angle was underwent an unusual change over 1173K. The contact angle first decreased and then increased. This phenomenon occurred due to the pinning of the Mg droplet at the triple junction. This change in the contact angle is an apparent change in contact angle. Therefore, the intrinsic contact angle is the initial value or the maximum value just before the disappearance of the droplet. The surface tension values were significantly affected by the molten magnesium set around the sample droplet at a lower temperature.

CD-1:IL05 **From Reactive Wetting to Reactive Brazing**
N. Eustathopoulos, SIMaP, Grenoble-Institut National Polytechnique, Saint Martin d'Heres, France

Good wetting is a necessary condition for joining by brazing alloys. Alumina is not wetted by conventional, non reactive metallic brazes. For this reason the standard industrial process to braze alumina to itself or to metallic solids involves Mo-Mn metallization and subsequent Ni plating of alumina surfaces prior to brazing. As this technique is complex and expensive, attempts are being made to eliminate the metallization step by using CuAg eutectic containing a few per cent of Ti. This element reacts with alumina to change in situ the interfacial chemistry thus modifying wetting and adhesion. The purpose of the presentation is to describe and discuss the thermodynamics and kinetics of reactive wetting and brazing in the CuAgTi/alumina system. Particular emphasis is given to evidence the effects of Ti concentration on the interfacial chemistry, joint microstructure and mechanical properties of copper / alumina assemblies. Results on the mechanical performances of Cu/alumina joints processed by reactive brazing are also compared with data obtained by the standard metallization route.

CD-1:IL06 **Dynamic Wetting Problem in Thermal Spray Process**
M. Fukumoto, Toyohashi University of Technology, Toyohashi, Japan

A variety of metallic and ceramic powder particles were thermally sprayed onto the mirror polished metallic substrate surface and the effect of both substrate temperature and ambient pressure on the flattening behavior of the particle was systematically investigated. In the flattening behavior of the sprayed particle onto the substrate surface, critical conditions were recognized both in the substrate temperature and ambient pressure. That is, the flattening behavior changed transitionally on that critical temperature and pressure range, respectively. A transition temperature, Tt, and transition pressure, Pt, were defined and introduced, respectively for those critical conditions. Three dimensional transition curvature by combining both transition temperature and transition pressure dependence was proposed as a practical and effective controlling principle of the thermal spray process. The fact that the dependence of both transition temperature and transition pressure on the sprayed particle material had similar tendency indicated that the dynamic wetting of the substrate by the molten particles seemed to be a domination in the flattening. Dynamic wetting problem on flattening behavior of individual particle in thermal spray process will be discussed in the talk.

CD-1:L07 Improvement in Wettability by Ultrasound and its Application to Cast Joining

Yoshiki Tsunekawa*, Masahiro Okumiya, Yuhichi Furukawa, Toyota Technological Institute, Nagoya, Japan

It is recognized that the apparent contact angle of a water droplet has decreased from a nonwetting to a wetting system on a paraffin-coated substrate with ultrasonic vibration. This physical phenomenon is based upon the forcible wetting due to the extremely high vibrational acceleration and the wetting hysteresis between an advancing and receding contact angle. Ultrasonic vibration is applied to overcome the main difficulties in cast joining such as an oxide film on a molten aluminum surface and pores adjacent to the solidified interface, which prevent the joining pair from its soundness. In order to eliminate an oxide film and pores at the interface, ultrasonic vibration is required to apply until the full remelting of the initially solidified aluminum alloy layer rapidly solidified by the direct contact of MMC. Ultrasonic vibration makes not only to accelerate the remelting, but also to disappear the thermal contact resistance between the joining pair. Resultantly, the sound interface with high strength is achieved through the ultrasonically improved wettability.

CD-1:L08 Characterization and Performance of Glass-ceramic Sealants for SOECs

H. Khedim[1]*, A.J. Connelly[1], E. Vernet[1], H. Nonnet[1], D. Coillot[2], L. Bruguière[1], [1]CEA, DEN, Marcoule, Bagnols-sur-Cèze Cedex, France; [2]UCCS - Unité de Catalyse et Chimie du solide, UMR CNRS 8181, Ecole Nationale Supérieure de Chimie de Lille, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq Cedex, France

Several glass-ceramic compositions based on three glass systems CAS (CaO-Al2O3-SiO2), SCAS (SrO-CaO-Al2O3-SiO2) and CASB (CaO-Al2O3-SiO2-B2O3) have been prepared and investigated. Thermal, chemical, and physical properties of the glass ceramics were examined along with the glass crystallization behaviour. Hot Stage Microscopy allowed observation of the sintering and wetting behaviour of glass-ceramics and showed it to be a highly complex process, significantly affected by glass composition variations, viscosity, glass transition temperature, crystallisation rate and the nature of the crystalline phases formed. The bonding characteristics of parent glasses with yttria-stabilized zirconia (YSZ) electrolyte, Macor® glass-ceramic and ferritic steel-based interconnect Crofer® were also observed under air and H2-H2O atmospheres at the cell operating temperature of 800 °C. Tightness tests have also been performed under thermal cycles between ambient to 800°C on selected compositions in order to confirm the seals ability to hold pressure over long time periods. The preliminary results are presented and discussed in this paper. They reveal the most suitable glass-ceramic compositions to meet the different criterions and the difficulties involved in formulating such a material.

CD-1:L09 In-situ HRTEM Observations of Spreading Reactive Molten Alloy on Ceramic Substrates

C. Iwamoto*, Dept. of Mechanical Engineering, Kumamoto University, Kumamoto, Japan; S.-I. Tanaka, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

Thus far, application of in-situ high resolution transmission electron microscopy (HRTEM) revealed the interface reaction between reactive brazing alloy and SiC at an atomic level. In this report, we applied the in-situ HRTEM technique to various substrates and compared the reaction process. Substrates used were carbon, Si, SiC, and Si3N4 wafer. Composition of the alloy foil was Ag-27.4 wt% Cu-4.9 wt% Ti. The foil was placed on the substrate and the combined specimen mounted on the heating holder of an HRTEM and heated in the microscope to a nominal temperature of approximately 1073 K. During the carbon brazing, nucleation and growth of nanoparticles are observed at the spreading molten alloy front. These particles were randomly oriented and their diameters were less than 10 nm. In case of the SiC brazing, SiC tended to dissociate along the polar planes and SiC nanoparticles nucleated at the polar planes. Crystallographic orientation relationship was observed between SiC and TiC nanoparticles. In contrast, in the case of reaction of Si and Si3N4, reaction phase formation was hardly observed.

CD-1:IL10 The Effect of Surface Adsorption on Substrate Wetting by Thermally Sprayed Particles

M.M. Hyland*, A.T.T. Tran, Department of Chemical and Materials Engineering, University of Auckland, New Zealand

The presence of mono- or multiple layers of adsorbed water or hydroxyl at the outermost layers of a surface has profound effects on the wetting and adhesion characteristics of a material. Such surface effects are manifested in many adhesion-related applications, including the deposition of ceramic and other engineering coatings by thermal spraying. In thermal spraying, the phenomenon of transition from undesirable, splashed coating droplets (splats) at low substrate temperatures to desirable disk shaped splats at higher substrate temperatures is strongly influenced by surface chemistry. We studied this by pretreating aluminium and steel substrates to generate surfaces with variable levels of physi- and chemisorbed water, and characterising the resultant morphologies and interfacial chemistries of NiCr plasma-sprayed splats. XPS was used to determine the temperature profile of water release from the substrate. The release of water from the conversion of surface oxyhydroxides to oxides coincides with typical transition temperatures above which disk splat formation is favoured. Surfaces with low oxyhydroxide contents produced predominantly disk splats; high oxyhydroxide contents gave splash splats. Modelling was used to show why this surface water release affects splat spreading.

Session CD-2

Theory, Modelling and Simulation of Interface Interactions

CD-2:IL01 Modeling the Effects of Surface Segregation on the Equilibrium Shape of FCC Alloy Crystals

D. Chatain*, CINaM- CNRS, Aix Marseille University, Marseille, France; P. Wynblatt, Department of Materials Science, Carnegie Mellon University, Pittsburgh, PA, USA

A simple model of surface segregation, which allows computation of both the energies and compositions of surfaces of different orientations, has been exercised in order to investigate the effects of segregation on the equilibrium crystal shape of fcc alloys. The parameters which control surface composition (namely the difference in surface energies of the pure components, the regular solution constant, and the solute misfit strain energy) have been varied over appropriate ranges. The results show that sufficiently deep energy cusps can develop at several surface orientations to produce facets that do not appear on the equilibrium crystal shape of pure fcc crystals.

CD-2:IL02 Thermo-chemical Design of Brazed Diamond-metal Joints

C. Leinenbach*, J. Wang, S. Buhl, M. Roth, EMPA - Swiss Federal Laboratories for Materials Testing and Research, Laboratory of Joining and Interface Technology, Dübendorf, Switzerland

Active brazing is an important method for joining diamonds to metals. The joint is realized by the formation of reaction layers between the diamond and the active filler metal and between the filler metal and the base metal. The structure, composition and thickness of these interlayers are important for the joint quality and are strongly influenced by the brazing temperature and time as well as of the composition of both the filler alloy and of the base materials. Finding the optimal brazing parameters is difficult and is widely done using trial-and-error tests. Thermodynamic modelling using the CALPHAD approach has proved to be a versatile tool for simulating interface reactions. In most of the recent works the reactions during brazing at only one interface were considered. In this contribution, a principal approach for the thermochemical design of diamond/metal joints based on CALPHAD simulations will be presented. For this, a self-consistent thermodynamic database for a Cu-based braze alloy system was developed. Kinetic simulations of interface reactions between the diamond diamond and the brazing alloy as well as between the brazing alloy and a steel were performed using the DICTRA software package. The simulation results were compared to results from real brazing tests.

CD-2:IL03 First-principles Theory and Atomistic Simulation of the Formation, Structure, and Stability of Incoherent Metal/ceramic Interfaces

A. Hashibon[1], C. Elsaesser[1], P. Gumbsch[1, 2]; [1]Fraunhofer Institute for

Mechanics of Materials IWM, Freiburg, Germany; [2]IZBS, University of Karlsruhe, Karlsruhe, Germany

First-principles calculations using density-functional theory (DFT), and atomistic simulations based on empirical interatomic potentials are used to study two different heterophase boundary systems. The first is the Cu/Al2O3 interface, which as a model case for metal-ceramic composites, has been subject to extensive experimental studies of electronic, mechanical and thermodynamic properties. DFT calculations were carried out to analyze the atomistic and electronic structures of coherent interfaces between Cu(111) and alpha-Alumina (0001) planes. A variety of interface models covering all high-symmetry configurations was considered. The second is the fcc-Cu/bcc-Ta interface system, which serves as a model case for heterophase interfaces between inorganic "soft" and "hard" materials. DFT calculations are used to study the adhesion and thermodynamic stability of thin Cu films on Ta (110) substrates. An interatomic potential, which extends embedded-atom-method (EAM) potentials to include angle-dependent terms, is used to study large-scale incoherent interfaces. Results for the equilibrium interface structure, the wetting behavior, and mechanical properties of these interfaces will be presented.

CD-2:IL04 **First-principles DFT Modelling of Interface Adhesion in Metal/Ceramic Systems**

C. Elsaesser, Fraunhofer IWM, Freiburg, Germany

Nanometer-sized thin-film or multi-layer structures of metal-oxide compounds are very attractive as potential alternatives to silicon-based components in integrated functional devices, e.g., dielectric thin-film capacitors for data storage, ferroelectric multi-layer stacks for electromechanical sensors or actuators, or transparent and conducting oxides in optoelectronics or photovoltaics. These metal oxide are in contact with metallic or oxidic electrodes. Upon miniaturisation in size, the properties of such components are increasingly influenced by atomistic and electronic structures at interfaces within the oxides or towards the electrodes. Experimental characterisation at the nanometer scale is usually rather difficult, and first-principles theory can provide augmenting, accurate and predictive, insight into interfacial adhesion-structure and structure-function relationships. This will be illustrated for metal/perovskite and perovskite/perovskite interfaces.

CD-2:IL05 **Link of Micro- and Macro- in Wetting Phenomena: DFT Modeling, Binding at the Interface and Contact Angle**

D. Fuks*, Sh. Barzilai, N. Froumina, N. Frage, Materials Engineering Dept., Ben Gurion University, Beer Sheva, Israel; E. Glickman, Physical Electronics Dept., Tel Aviv University, Tel Aviv, Israel

Reaction wetting of ceramics by liquid metals can result either from chemical reactions that form new phase at the solid-liquid (SL) interface, or from adsorption of the reactive element at this interface. Significant reduction of equilibrium contact angle due to alloying In with only 1.5 at % Ti was observed recently in the system CaF2- liquid (In + Ti) in the absence of conclusive evidence of Ti-rich phase formation at the SL interface. This suggests a possible role of Ti adsorption as the reason for wetting improvement. The effect of Ti additions on the wetting behavior of In-Ti and Sn-Ti alloys on the CaF2 substrate is clarified by DFT calculations. We combined the nearest neighbor approximation for regular solutions with the ab-initio calculation technique to estimate the surface coverage by Ti and the corresponding decrease of SL energy caused by Ti adsorption on the F-terminated CaF2 in contact with In. Potential role of high detachment barriers which can prevent fast Ti diffusion and adsorption on the fluorite free surface , as well as the role of fluorite evaporation, are also discussed.

Session CD-3
Advances in Joining Methods and Materials

CD-3:IL01 **Ultrarapid Transient-liquid-phase Bonding of Advanced Ceramics**

Sung M. Hong, Christopher C. Bartlow, Thomas B. Reynolds, N. Saito, Andreas M. Glaeser*, Department of Materials Science and Engineering University of California, Berkeley, CA, USA

To expand the use of advanced ceramics, it is necessary to develop rapid, reliable, and economical methods that allow complex structures to be assembled easily from simpler parts. Transient-liquid-phase (TLP) bonding has the potential to merge the best features of liquid-state and solid-state joining processes. The presentation will report on the use multilayer Ni/Nb/Ni and Co/Nb/Co interlayers to bond Al2O3 and Al2O3-based composites, specifically ZrO2-toughened Al2O3 (ZTA). Combining thin layers of Ni or Co with thick Nb foils in a multilayer architecture allows thin, Nb-rich liquid films to develop between a solid Nb core layer and the Al2O3(-based) ceramic. Wetting studies show that the resulting liquid exhibits an unusually low contact angle that promotes filling of interfacial gaps. Rapid diffusion of both Ni and Co in Nb allows for rapid liquid-phase disappearance, rapid interlayer homogenization, and the development of interlayers with remelt temperatures >2000°C during isothermal holds as short as 5 min at 1400°C. We have achieved reproducible joint strengths; in most cases, the failure of joined assemblies involves ceramic failure, and strengths are limited by the ceramic, not the joint. The effects of Al2O3 characteristics and processing conditions will be discussed.

CD-3:IL02 **Joining Ultra-high-temperature Materials: Ceramic/ Metal Interfaces in Reactive Brazes**

J. Ernesto Indacochea*, Oscar Quintana, University of Illinois at Chicago, Chicago, IL, USA

Important physical and mechanical properties of new advanced dissimilar materials in different applications are strongly affected by the structure and properties of interfaces. Metal-ceramic interfaces are essential in brazing ceramics to metals, producing ceramic metal composites, in electronic packaging systems, and in thin film technology. Often the bonding and adhesion between the ceramic and the metal is critical to the performance of a component. Solid Oxide Fuel Cells (SOFC's) are among energy conversion systems particularly appealing because they are environmentally benign; however the sealants are critical in SOFC development. The objective in this investigation is to seal yttria stabilized zirconia (YSZ) electrolyte to stainless steel in the electrical interconnect or gas manifold which is exposed to elevated temperatures (500-1000 °C). In this presentation the interfacial reactions and interfacial structure between the YSZ and type of filler metal are discussed. The ceramic substrate was bonded to itself and to Crofer-22APU®. Two filler metal commercial alloys, Ti-Ni alloy (TiNi67®) and Ag-Cu-Ti alloys (Ticusil®, and Cusil-ABA®) were used. Brazing with TiNi67® was done at 1010 °C and at 900 °C with the Ag-Cu-Ti alloys. Brazing was done for 15, 30 and 60 min in vacuum. Analytical techniques, such as synchrotron X-ray diffraction X-ray powder diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy were utilized to examine the YSZ/filler metal interface. With the Ag-Cu-Ti filler metals, Ti segregated to the interface and formed a TiO interlayer allowing wetting and further bonding. With the Ti-Ni alloy, Ti dispersed uniformly through the braze and a TiOx interlayer was detected at the interface.

CD-3:IL03 **Development of Joining Technique for SiC/SiC Composite Component Utilizing NITE Process**

T. Hinoki*, Y.H. Park, S. Konishi, Kyoto University, Uji, Kyoto, Japan

Silicon carbide (SiC) can be used in extremely harsh environments due to its excellent mechanical properties and chemical stability even at high temperature. The novel process called Nano-powder Infiltration and Transient Eutectic-phase (NITE) Process has been developed based on the liquid phase sintering process modification. Very dense and highly crystalline SiC/SiC composites can be fabricated by NITE process. The joining technique using the same SiC nano-powder and sintering additive as with NITE processing was developed. It was also possible to cut screw without chipping due to dense feature and excellent fracture toughness. The scale model for compact intermediate heat exchanger was fabricated using NITE-SiC/SiC composites. The composite plates with 10 cm square and 6 mm thickness were grooved for cooling channels with 5 mm width and 4 mm height. Five composite plates including the three plates with cooling channels were joined by hot pressing. The scale model was joined with four composite tubes by screw joint and hermetic seal. Present study is the result of "Development on Compact Intermediate Heat Exchanger Using Advanced Composite Material" entrusted to "Kyoto University" by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

CD-3:IL06 **Reactive Air Brazing (RAB): A Novel Joining Technique for High-temperature Electrochemical Applications**

J. Hardy*, J.Y. Kim, K.S. Weil, Pacific Northwest National Lab., Richland, WA, USA

As interest in high-temperature electrochemical devices such as solid oxide fuel cells (SOFC's) has increased, there have been tremendous needs to develop an appropriate joining technique, which provides hermetic seal and proper strength between ceramic-ceramic and ceramic-metal parts under operating conditions. A novel technique referred to as reactive air brazing (RAB) has shown a promise in the joining of components used in high-temperature applications. Similar to active metal brazing technique, the reactive component in the RAB is reactively to modify oxide faying surfaces, improving the wettability with the oxide and potentially increasing bond strength between braze and ceramics. The most important advantage of RAB over conventional active metal brazing is that joining operation of RAB technique can be conducted in oxidizing atmosphere since oxide is used as reactive species. In this presentation, the properties and microstructure of various RAB brazes will be discussed.

CD-3:IL07 Wetting and Joining in Transition Metals Diborides

M.L. Muolo*[1], F. Valenza[1], N. Sobczak[2], A. Passerone[1], [1]IENI-CNR, Genova, Italy; [2]Foundry Research Institute, Cracow, Poland

The transition metals diborides, due to their physico-chemical and mechanical properties, are excellent candidates for applications in extreme environments. As they can be used as bulk self-standing materials, or supported by metallic structures, their joining to obtain complex shapes or to realize metal/ceramic structures, is of the utmost importance. As brazing processes are governed by the basic wetting characteristics of the phases involved, we have undertaken a wide program to study the wetting of sintered (Ti,Zr,Hf) diborides by molten metals and alloys in the temperature range of 1000-1500 °C. Results will be reviewed concerning the evolution of contact angles with time, temperature and concentration of the liquid phases. Interfacial phenomena like reaction and dissolution are interpreted on the basis of newly computed ternary phase diagrams. Moreover, for the first time, the ab-initio modeling technique DFT, has been used to evaluate the adhesion of Ag and Au on ZrB_2, finding a good agreement with experimental data. Joining tests of ZrB_2 and HfB_2 to each other and to alloys of relevant industrial interest have also been performed, using the filler alloys developed on the basis of the previous wetting studies. The joint strength has been evaluated by shear tests.

Session CD-4
Residual Stresses, Joint Modeling Design, Characterization and Analysis

CD-4:IL01 Mechanical Properties and Residual Stress in Hermetic Feedthroughs for Medical Devices

M.W. Reiterer*, Medtronic Strategy and Innovation, Medtronic, Inc., Minneapolis, MN, USA; B. Tischendorf, W.J. Taylor, A.J. Thom, Medtronic Energy and Component Center, Medtronic, Inc., Brooklyn Center, MN, USA

Implantable medical devices, such as cardiac pacemakers and neuro-stimulators, are typically comprised of a titanium can, electronic components on the inside and a connector on the outside. While maintaining a hermetic seal and electrical insulation the electrical connection between the two environments is facilitated by feedthroughs (FTs). Both brazed ceramic and glass FTs are utilized in Medtronic devices, and biocompatibility and long term reliability are of utmost importance to ensure functionality and deliver essential therapy to the patient. Due to their nature FTs are small, multi-material composites with typically significant mismatch of thermal expansion and different mechanical properties. The investigated brazed and glass FTs are thermally processed and develop significant residual stresses during cooling. Knowledge of the stress state is very important, as it can have both positive and negative impact on FT performance and reliability. A combination of analytical, experimental and numerical methods, developed and routinely applied at Medtronic to improve the fundamental understanding of metal to ceramic joints, is discussed, and an outlook of promising techniques is presented.

CD-4:IL02 Measured Residual Stress/Strain Distributions in a Micro-Area around a Ceramic/Metal Interfaces

Shun-ichiro Tanaka, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

Experimental efforts in author's laboratory to measure the actual stress/strain in a micro-area around ceramic/metal interfaces are reviewed. The measurement methods being developed and applied are X-ray micro-sin2ψ method, surface acoustic wave, micro-Raman scattering, micro-FTIR and convergent beam electron diffraction (CBED) in TEM. These methods provide tools to evaluate the actual stress/strain quantitatively in a micro-area for all material. The diameter of measured area ranged from sub-millimeters to nanometers, and the smallest diameter we successfully measured the stress/strain is 25 nm by CBED. Examples of the measured stress/strain distributions around the interface are shown in the followings: (1) residual stresses around brazed interfaces of Si3N4/Cu/steel compared with results of 3D-FEM analysis, (2) depth profiles of the residual stress at the joined interface. In the first interface, I found the maximum points of a principal stress in the Si3N4 part 0.5 mm from the edge which matched well with the predicted crack initiation points in a thermal shock test, whereas stress maximum was detected in the center of the interface different from the FEM analysis. The effects of residual stress/strain on the physical and chemical properties of the materials are also shown.

CD-4:IL03 Recent Advances in Joining of SiC Based Materials

M. Salvo*, V. Casalegno, M. Ferraris, S.Han, S. Rizzo, A. Ventrella, Politecnico di Torino, Dipartimento di Scienza dei Materiali e Ingegneria Chimica-DISMIC, Torino, Italy

SiC based materials have brittle nature and consequent poor workability which limit their extensive use. In order to avoid this limitation, joining of small parts is employed to obtain the final components: for this reason, joining of SiC based components is a true issue in Materials Science and Technology. Recent advances in the joining of SiC-based materials will be reviewed, both for ceramic/ceramic and ceramic/metal joints; joining materials such as brazing alloys, glasses or composites will be summarised with particular concern to their mechanical tests. Various experimental test set up can be found in the literature to estimate the shear strength of a joint. Even though asymmetrical four point bending test is the only one recommended by the ASTM for obtaining a pure shear strength of joined advanced ceramics, single-lap or offset single-lap tests in compression are widely used methods to obtain an apparent shear strength. A completely different testing method is torsion: with it, a pure shear strength can be measured without the limitations in the joining material strength. The presence of many different shear strength tests in the literature makes a comparison quite impossible: this issue will be discussed together with the experimental results of a wide testing campaign.

CD-4:IL04 Residual Stress Measurement around the Interface of Copper Bi-crystal Developed by Uniaxial Extension

Takao Hanabusa[1]*, Ayumi Shiro[2], Tatsuya Okada[1], [1]Institute of Technology and Science, The University of Tokushima, Tokushima, Japan; [2]Graduate School of Advanced Technology and Science, The University of Tokushima, Tokushima, Japan

Crystal deformation is affected by grain boundaries in polycrystalline materials. As a result of dislocation pile-up at the boundaries, micro residual stresses develop near the boundaries. In this study, the basic study on the boundary constraint was investigated from the view point of residual stress formation near the grain boundary. A copper bi-crystal specimen with 90 degrees tilt boundary was deformed in tension. After the plastic extension of 30%, deformation bands developed in a deformed matrix along the grain boundary. The residual stresses were focused in the deformed matrix and the deformation band. Residual stresses were evaluated by the X-ray single crystal measurement method by using synchrotron radiation of SPring-8 in Japan Synchrotron Radiation Research Institute. Pole figures were used to determine crystal orientations in deformed regions. The observation showed that crystal orientations are different between the deformed matrix and the deformation band. Residual stresses in the direction along the grain boundary in deformed matrix were compressive whereas those in the deformation band were tensile. Residual shear stresses were in an opposite state between the deformed matrix and the deformed band.

CD-4:IL05 Preparation, Characterization and Applications of Glass-ceramic-to-metal Seals

I.W. Donald*, B.L. Metcalfe, L.A. Gerrard, P.M. Mallinson, J.A. Fernie, Materials Science Research Div., AWE, Aldermaston, Berkshire, UK

There has, in recent years, been a revival of interest in glass-ceramic-to-metal seals. This has been driven in part by the development of sealants for SOFCs, coupled with a requirement for more complex, miniature, and light-weight electrical and electronic components. It is recognized that many factors need to be taken into consideration in the successful design and manufacture of high quality glass-ceramic-to-metal seals, particularly if an adequate component lifetime is to be achieved. During their preparation, undesirable reactions may occur between diffusing metal species and glass constituents, and these can lead to the formation of highly localized internal stresses, the presence of which can initiate failure of a seal either during manufacture or, more seriously, whilst in service due to the influence of static fatigue. In the case of high temperature systems, reactions under hostile operating conditions also need to be taken into consideration. A thorough understanding of the relevant glass-ceramic/metal interactions is therefore required in order that steps can be taken to avoid or at least minimize reactions within the interfacial region that may lead to localized modifications of the glass-ceramic microstructure. In this contribution, factors influencing the lifetime behaviour of glass-ceramic/metal systems are reviewed and discussed, with particular reference given to components developed at AWE including seals to stainless steels, Ni-based superalloys, and Ti alloys. Fundamental studies on bonding to pure Fe, Ni and Cr and the corresponding binary alloys are also included.

CD-4:IL06 **The Quality of Brazed Ceramic and Cemented Carbide Joints - A Mechanical and Metallurgical Assessment**

W. Tillmann*, L. Wojarski, Institute of Materials Engineering, TU Dortmund, Dortmund, Germany

In order to exploit the full potential of ceramic materials it is inevitable that adequate joining technologies are available. A comparable situation is found regarding joints between cemented carbides and counterparts. Such joints are not easy to manufacture due to wetting and bonding problems as well as owing to induced thermal stresses. Currently active brazing is a potential approach for fabricating such joints. The filler alloy contain reactive agents such as Titanium or Hafnium etc. that are to interact forming wettable reaction layers on the ceramic surface. It goes without saying that they function very well on cemented carbides too. The paper describes potential wetting and bonding reaction from a metallurgical point of view. Ceramics, superabrasives and cemented carbides are investagted with respect to interfacial reactions. The quality of the reaction products is of crucial importance regarding the mechanical performance of the joints as their imanent brittleness can lead to a significant weakening. Apart from metallurgical assessment mechanical tests are conducted in order to deliver data for their integration in hdybride structures. FE methods can be applied to assess the stress situation in the final joint. Thus it is possible to adjust the design accordingly.

CD-4:IL07 **Design and Characterization of Metal-ceramic Joints for High Temperature Applications**

N. Sobczak[1]*, R. Asthana[2], M. Singh[3], [1]Centre for High Temperature Studies, Foundry Research Institute, Cracow, Poland; [2]Department of Engineering & Technology, University of Wisconsin-Stout, Menomonie, WI, USA; [3]Ohio Aerospace Institute, NASA Glenn Research Center, Cleveland, OH, USA

The paper discusses recent developments in joining dissimilar materials by liquid-assisted processes. Special attention is paid to the design and characterization of metal-ceramic joints for high-temperature applications, including ultra high temperature ceramics and advanced C-C and SiC-SiC composites. The results of improved high-temperature sessile-drop wettability tests coupled with *in situ* opening of the metal/ceramic interfaces at test temperature by applying recently developed procedures (pushing drop, sucking drop, tilting drop) are visualized in order to demonstrate the complex wetting and spreading behavior responsible for metal-ceramic bonding. The effects of mutual dissolution of contacting materials, the type and morphology of reactively formed interfacial products, reactive metal penetration and the formation of gaseous products are evidenced. Practical recommendations for the design of metal-ceramic joints for high-temperature applications are given for selected groups of materials.

CD-4:IL08 **Modelling and Computer Simulation of Residual Stresses at Joined Interfaces**

S. Schmauder, Institute for Materials Testing, Materials Science and Strength of Materials (IMWF), University of Stuttgart, Stuttgart, Germany

In this contribution, results are presented of the influence of residual stresses in metal matrix composites and at joined interfaces resulting in damage initiation in the particles, interfaces and in the matrix material. In addition, the influence of a thin or thick brittle or ductile interphase between the constituents is taken into account in the numerical analysis. The simulation results show that the damage behaviour of the composites is strongly dependent on the failure behaviour of all three phases involved. It is found that the more ductile the interphase the stronger the MMC resistance against damage evolution. In this respect it seems to be important to control the interphase strength to being more ductile than that of the matrix. A brittle interphase however results only in improved failure resistances when this phase shows superior strength values as compared to the ceramic particles. The results are found to depend on residual stresses as a function of thermal expansion mismatch and processing cooling interval to a more or less extent depending on the ratio of internal versus applied stress ratio with a stronger impact when the residual stresses are comparable in height as the external stresses.

CD-4:L09 **Temperature Modeling for Friction Welding Process Between Ceramic and Metal**

Hazman Seli*, Ahmad Izani Md. Ismail, Endri Rachman, Zainal Arifin Ahmad, Universiti Sains Malaysia (USM), School of Matls Eng, Penang, Malaysia

Numerical model of friction welding between ceramic and metal rods are established to predict temperature rises during the initial phase of the process. In this study alumina(ceramic) and mild steel(metal) rods are used and joined with aluminium sacrificial interlayer. The workpieces are welded together by holding alumina still, while rotating the steel attached with aluminium piece under influence of an axial load which creates frictional heat in the interfaces. The transient thermal response in welding is hard to model analytically. Generally, heat is dissipated over time scales of less than two seconds. For the thermal model, an explicit one dimensional (1-D) finite difference (FD) method is utilized to approximate the heating and cooling temperature distribution of the joined dissimilar rods. The preliminary predictions are compared to actual thermocouple data from welds conducted under identical conditions and are shown to be in fair agreement. Even though the FD method proposed in this study cannot replace a more accurate numerical analysis, it does provide guidance in weld parameter development and allows better understanding of the friction welding process.

Poster Presentations

CD:P01 **Finite Element Modeling of Thermal Stress in ITER Prototype Optical Windows and its Influencing Parameters**

Marijke Jacobs[1, 2]*, Guido Van Oost[1], Joris Degrieck[1], Ives Debaere[1], Andrei Goussarov[2], Vincent Massaut[2], [1]Ghent University, Ghent, Belgium; [2]SCK·CEN, Mol, Belgium

Glass-metal joints are needed for the optical windows in ITER to perform diagnostics. These joints must be leak tight for the safety (presence of tritium in ITER) and to preserve the vacuum. They must also withstand the ITER environment: temperatures around 250 °C and neutron fluxes of 10^9 n/cm^2.s. At the moment, little information is available about glass-metal joints suitable for ITER. Therefore, we set-up a 2D elastic model of prototype Al diffusion bonded optical windows using Abaqus code to model temperature effects on the windows. With this model we analyzed the influence of different parameters like the joint area and the braze thickness on the mechanical properties of the joint. Calculations of the thermal stress created by a temperature field of 150 °C (normal ITER temperature) showed that the Al-bond is the weakest part of the windows. To find a way of reducing the thermal stress, the influence of some parameters has been studied. In particular, depending on the prototype geometry, a specific thickness of the Al layer can result in a minimum of stress in the Al bond while the joint area and the thickness of the glass have only a small influence on the stress in the windows. The calculations allowed to propose an optimized design for the windows prototypes.

CD:P02 **Interfacial Microstructure and Properties of (SiC / SiC) Joint brazed with Ag-Cu-Ti Alloys**

A. Nemati, Department of Material Science & Eng., Sharif University of Technology, Tehran, Iran; A.h. Ghazi Daryani*, Researcher in Ceramic Group, Department of Material Science & Eng., Sharif University of Technology, Tehran, Iran; A.h. Kokabi, Department of Material Science & Eng., Sharif University of Technology, Tehran, Iran

Our results indicated the possibility of SiC-SiC joint in an inert environment using Ag-Cu -Ti alloys in which Ti acts as an active component. The heating and cooling conditions must be optimized to obtain a proper joint. The results showed that the joint character was improved with increase of temperature and time. The optimal conditions were suggested to be 900 °C for 90 minutes. The results showed that the Electrical Resistivity of the samples was increased with temperature & time, but the variation was not significant. The microstructure showed an excellent bonding at the interfaces, but the joint was deteriorated with increasing of temperature and time.

Symposium CE

CERAMICS AND COMPOSITES IN EXTREME ENVIRONMENTS

Oral Presentations

Session CE-1
Ultra High Temperature Ceramics

CE-1:IL01 **Material Properties Improvement in Ultra High Temperature Ceramics via Microstructure Tailoring**

Guo-Jun Zhang, State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Shanghai, China

Ultra high temperature ceramics (UHTCs) with chemical and physical stability at high temperatures (e.g., above 2000 °C) and in reactive atmospheres (e.g., monatomic oxygen) are key materials for applications in liquid/solid rocket engines and thermal protective systems of hypersonic flight (nose cones and leading edges). In this work refractory diborides and carbides including ZrB2, HfB2, ZrC, HfC and TaC were investigated and characterized by tailoring the material microstructures. For example, diboride-silicon carbide composites with platelet-shaped diborides in the microstructures have been developed, and the materials demonstrated much improved mechanical properties. On the other hand, highly textured ZrB2-SiC and HfB2-SiC ultra-high temperature ceramics with c-axis orientation were prepared via strong magnetic field alignment (SMFA) during slip casting, followed by spark plasma sintering. Results showed that hardness on SS surface (perpendicular to magnetic field) was superior to that on TS surface. Oxidation resistance demonstrates obvious anisotropy. The anisotropic properties of the textured materials would provide an opportunity to the material design and selection of UHTCs. Compared with the textured ZrB2-based ceramics, the textured HfB2-SiC ceramics shows much better oxidation resistance. Other textured UHTCs, for example, ZrB2-MoSi2 ceramics, will also be reported.

CE-1:IL02 **Ceramics for Aeropropulsion Applications**

Eric J. Wuchina*, Mark M. Opeka, Naval Surface Warfare Center, West Bethesda, MD, USA

The 21st century has ushered in a new, exciting era of hypersonic flight. Hypersonic vehicles (including sub-orbital and earth-to-orbit vehicles) are being considered for rapid global and space access missions. As higher flight speeds produce higher vehicle surface temperatures, the need for new materials has become imperative. Hypersonic vehicles with sharp aerosurfaces, such as engine cowl inlets, wing leading edges, scramjet combustion chambers, and nosecaps, have projected needs for 2000 to 2400 °C materials which must operate in air and potentially be re-usable. At this time, there are few, if any, off-the-shelf materials to meet these future hypersonic thermal protection system (TPS) needs. The development of ultra-high temperature ceramics, or UHTCs (typically transition-metal borides, carbides, and nitrides), are of considerable engineering importance due to their high melting temperatures (>3000 °C) and high strength at use temperatures. Oxidation resistance and thermal shock behavior are considered extremely important properties necessary to meet the high heating rates and lifing requirements seen in many hypersonic structural applications. Recent advances in processing and mechanical properties in monolithic single and multiphase materials have been widely reported in the community. One of the main focus areas has been the understanding and improvement of the oxidation behavior of this class of materials, with much of the focus being on boride based systems. In this paper, we will discuss the issues involved with the design of structures from monolithic brittle materials and the use of oxidation-protection coatings. New directions in materials R&D will be covered, including preceramic polymer precursors for use in the development of UHTC-based CMCs, high-temperature cermets, and structural insulators. The status of recent Navy development of oxidation-resistant materials, with a focus on work in the Hf-Ta-N system, will also be presented.

CE-1:L03 **Oxidation Mechanism of ZrB2-SiC in a Solar Furnace Above 2200 °C**

A.-S. Andreani[1]*, A. Poulon-Quintin[2], F. Rebillat[1], [1]Laboratoire des Composites Thermostructuraux , UMR 5801 CNRS-Snecma-CEA-UB1, Pessac, France; [2]Institut de Chimie de la Matiere Condensee de Bordeaux, CNRS UPR 9048, Pessac, France

An original method for testing ultra-high-temperature ceramics (UHTC) at very high temperature (superior to 2200 °C) in air with an exposure time of several minutes is used here. The solar furnace is a heating system based on concentrated light radiance supplied by the sun for the heating of material surface. The direct solar flux varies from 800 W/m2 up to 1050 W/m2 with a homogeneous surface radiation of 13 mm2. This method enables a large temperature-time composition parameter space to be covered by rapidly producing a large set of oxidized samples. Massive cylindrical specimens of UHTC material are prepared by spark plasma sintering at 1900 °C under a pressure of 100 MPa for 5 minutes. Thanks to this method, samples are tested at a temperature superior to 2250°C for 5 minutes in air. The complex oxide scale known to form during oxidation of ZrB2+SiC (20%vol) material is shown to be easily reproduced using this method. It consists of a thin outer silica layer and zirconia columnar layer with the region of SiC depleted zone in ZrB2 phase.

CE-1:L04 **Measurements of Cation and Anion Diffusion in Aluminum Oxide with ToF-SIMS**

T. Nagakawa, National Institute for Materials Science, Tsukuba, Japan; J.D. McGuffin-Cawley*, A.H. Heuer, Case Western Reserve University, Cleveland, OH, USA

Self-diffusion in alumina has been studied for 50 years using cation and anion tracers. The techniques available to resolve tracer concentration profiles have evolved markedly through these decades. Early experiments were limited to determining the total tracer uptake that occurred during a diffusion anneal (i.e., the integral of the concentration profile). Later nuclear reaction analysis (NRA) and then secondary ion mass spectroscopy (SIMS) allowed determination of one-dimensional concentration gradients. In particular, SIMS offers high depth resolution. However, these methods still integrate over hundreds of square microns in the plane parallel to the surface of the specimen and thus are unable to resolve heterogeneous tracer profiles due to either non-uniform deposition or rates of diffusion. Frequently researchers have had to make assumptions of “high diffusivity paths” to explain the occurrence of non-Fickian concentration profiles. ToF-SIMS offers several distinct advantages, notably parallel collection of data and high lateral resolution, in fully resolving concentration gradients in three dimensions. Results of experiments will be presented and discussed in light of prior work.

CE-1:L05 **Oxidation of ZrB2 Ceramics with Tungsten Carbide Additions**

Shi C. Zhang*, Greg E. Hilmas, William G. Fahrenholtz, Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, Missouri, USA

The effect of tungsten carbide (WC) content on the oxidation resistance of zirconium diboride (ZrB2) was studied. A previous study showed that 4 mole% WC improved the oxidation resistance of ZrB2 ceramics by promoting the liquid phase sintering of the zirconia (ZrO2) scale formed during oxidation. To optimize the WC content, ZrB2 ceramics were prepared with WC additions ranging from 4 to 16 mole%. The ceramics were pressurelessly sintered to near full density. The effect of WC content on the oxidation resistance was studied by measuring weight gain and the thickness of the oxide scales formed during isothermal furnace oxidation at 1500 °C and 1600 °C. Due to the solid solution limit of W in ZrB2, WC additions were later limited to the range of 4 to 6 mole%. Additions of 4 and 6 mole% WC reduced both the weight gain and oxide scale thickness, compared to nominally pure ZrB2 (0 mole% WC). After oxidation of nominally pure ZrB2 at 1600 °C for 3 hours, the mass gain was 27 mg/cm2 and the oxide layer thickness was 800 µm. The addition of mole% WC reduced the weight gain to 6.0 mg/cm2 and the oxide layer thickness to 310 µm. Further reductions in weight gain, to 4.3 mg/cm2, and oxide layer thickness, to 110 µm, were achieved for a 6 mole% WC addition.

CE-1:IL06 Mechanical and Electrical Properties of AlN-SiC Solid Solutions

Junichi Tatami*, Ryota Kobayashi, Toru Wakihara, Katsutoshi Komeya, Takeshi Meguro, Yokohama National University, Yokohama, Japan; Tu Rong, Takashi Goto, Tohoku University, Sendai, Japan

AlN-SiC solid solutions were fabricated by SPS technique. The relative density of the samples was over 99% and the phases present were 2H and 6H. The highest values of the bending strength and the fracture toughness at room temperature were 1GPa and 5MPam$^{1/2}$, respectively. The bending strength at the temperature of 1700 ^{O}C was over 400MPa. The SPSed samples were heat-treated to fabricate single phase of dense AlN-SiC solid solutions. The samples of 50mol% AlN and 75mol% AlN heat-treated at 2200 and 2100 °C for 3h were changed into 2H single phase. The grain size increased as formation of solid solutions. The single phase AlN-SiC solid solutions were insulator. In order to control p-type conduction, the small amount of excess Al and C was added. As a result, Al and C additives improved the electrical conductivity. In particular, the electrical conductivity of the sample of 50mol% AlN by adding 3mol% Al_4C_3 was over 100S/m at 300 °C. Because Seebeck coefficient was positive, the AlN-SiC solid solutions were confirmed to be p-type semiconductor.

CE-1:IL07 Transparent Alumina for MWIR Windows and Domes

M.R. Pascucci*, M.V. Parish, CeraNova Corporation, Marlborough, MA, USA

Missile domes are one of the most demanding applications for ceramics. Materials used for missile domes and windows serve a dual purpose - they protect the sensors from harsh environments while simultaneously transmitting useful radiation to the sensor. Critical properties for these materials include high strength and high thermal shock resistance which enable domes and windows to withstand high aerodynamic forces, severe aerothermal heating, raindrop impacts, and sand erosion. In addition, high transmission over a broad wavelength range in the infrared is essential. CeraNova's transparent alumina (CeraLuminaT) has sub-micron grain size (300-500nm) and high transmittance in the mid-wave infrared. High purity nanopowders are used to produce fully dense, fine grain alumina which possesses significantly improved properties when compared to both larger grained alumina and single crystal sapphire. In addition to high transparency, the fine, uniform grain size of CeraLuminaT imparts high hardness, high strength, and high thermal shock resistance. The effects of grain size on optical, mechanical, and thermal properties will be presented.

CE-1:L08 Synthesis and Characterization of Multi-walled Carbon Nanotube Reinforced Tantalum Carbide Composites via Spark Plasma Sintering

Srinivasa Rao Bakshi, Vishal Musaramthota, Arvind Agarwal*, Plasma Forming Laboratory Nanomechanical and Nanotribological Laboratory, Department of Mechanical and Materials Engineering, Florida International University, Miami, FL, USA

Multi-walled carbon nanotubes (CNTs) reinforced tantalum carbide (TaC) composites were prepared by spark plasma sintering (SPS). Four (4) wt.% CNTs were added to TaC so that the over all composition was a little higher than the high carbon eutectic phase in Ta-C phase diagram. Two kinds of CNTs, one with short length (1-3 µm) and other with long length (10-20 µm) were used. CNTs were added to supply excess carbon for eutectic phase formation as well as to improve the mechanical properties. Effect of temperature (1800 °C and 2200 °C) in SPS on the densification was studied. CNTs were dispersed nicely in fine sized TaC powders (<1 µm dia.) by ultrasonic mixing in a liquid medium. TaC-CNT composites were synthesized with and without 1 wt.% B4C added as a sintering aid. The density and microstructural features of the TaC-CNT composites were studied using optical microscopy, X-ray diffraction and scanning electron microscopy. Mechanical properties like elastic modulus and hardness were measured using nanoindentation and fracture toughness was measured using micro-indentation technique.

CE-1:L09 Microstructure and Toughening Mechanisms of Reinforced ZrB2-based Ceramics

D. Sciti*, L. Silvestroni, V. Medri, S. Guicciardi, CNR-ISTEC, Institute of Science and Technology for Ceramics, Faenza, Italy

In the last five years, research on Zirconium diboride-based materials has focused on fabricating high density composites possessing good strength. However, the low fracture toughness remains one of the major concern for the application of these materials under severe environment. In this work, starting from a ZrB2 matrix, composites containing various types of reinforcement such as SiC whiskers, SiC chopped fibres, are produced. Their microstructural features are investigated by SEM and TEM techniques. The mechanical properties are compared to those of the reference unreinforced material to assess the real variation obtained by introduction of these reinforcing agents. Following the inspection of the crack/microstructure interaction, the experimental fracture toughness is quantitatively compared to theoretical models. The addition of whiskers to ZrB2 allows both strengthening and toughening compared to the reference material. In the fibre-reinforced composites, the increase in fracture toughness is instead accompanied by a decrease of strength. At 1200 °C, a strengthening effect is obtained independently of the reinforcement type.

CE-1:L10 Study of the Spark Plasma Sintering Behaviour of Microsized and Nanosized Zirconium Oxycarbide (ZrCxOy) Powders

J. David*, M. Gendre, A. Maître, G. Trolliard, B. Soulestin, Laboratoire Sciences des Procédés Céramiques et Traitements de Surface, UMR CNRS 6638, UFR Sciences et Techniques, Limoges Cedex, France

The zirconium oxycarbide (ZrCxOy) is part of the most refractory ceramics since its melting point is close to 3450 °C. However, the strongly covalent nature of the zirconium-carbon boundings in oxycarbides makes difficult their sintering starting from powders. In this context, the use of both Spark Plasma Sintering, which allows high heating rates and short isothermal dwells and, nanosized starting powders can lead to obtain full dense monoliths keeping fine microstructures. Two different ways of oxycarbide powder synthesis have been compared in order to elaborate dense monoliths by SPS. First, microsized powders ($\phi m = 0.5 \mu m$) of ZrCxOy were synthesized using the classical solid-solid reaction of commercial zirconia carboreduction route in dry way. Second, nanosized powders of oxycarbide (<100nm) were elaborated by carboreduction from stabilized aqueous slurry of nanosized zirconia particles and saccharose as a carbon source. SPS behaviours of the different granulometries of oxycarbides powders were analysed to elucidate the influence of oxycarbide grain size (micro and nanometric) on the sintering reactivity and, on the final (micro-)structural features of SPSed samples.

CE-1:IL11 ZrB2-Based Ceramics for Ultra-High Temperature Applications

William G. Fahrenholtz*, Gregory E. Hilmas, Missouri University of Science and Technology Rolla, MO, USA

Research related to ultra-high temperature ceramics, including zirconium diboride (ZrB2), has experienced a resurgence in the past ten years. All aspects of ZrB2 have been investigated including synthesis, forming, densification, properties, and performance. Notable research accomplishments at Missouri S&T include producing ZrB2-SiC ceramics with the highest reported room temperature strengths, developing pressureless densification processes for ZrB2 and ZrB2-SiC, and improving the thermal shock resistance of ZrB2-based ceramics using engineered architectures. More recently, research has examined thermal stress development, oxidation resistance, and the influence of impurities on elevated temperature thermomechanical properties of ZrB2-based ceramics. This presentation will focus on the most recent results in our laboratories in these areas.

CE-1:L13 Creep of Single Crystal ZrB2 Using Non-contacting Methods

R.W. Hyers[1], R.P. Aune[2], K.W. White[2]*, [1]University of Massachusetts, Amherst, MA, USA; [2]University of Houston, Houston, TX, USA

As a primary candidate for ultra-high temperature applications, little data exists on the microstructural constituent behavior of ZrB2 or its composites, particularly when subjected to elevated temperature under sustained loading. This single crystal creep study will serve as the first step toward future micromechanical and atomic-scale modeling studies on the high temperature fracture and creep behavior of complex microstructures of ZrB2 composites. The experiments were performed using the ESL facility at NASA Marshall Space Flight Center (MSFC) in Huntsville, AL. This novel apparatus is capable of levitating the sample under a high vacuum (≈10-8 mbar) and elevated temperatures. The 2 mm sample is rotated by the photon pressure exerted from a laser to cause creep deformation due to the centripetal acceleration. The deformation is analyzed using image processing methods, detailed previously by one of the authors (RWH). The results will be analyzed in terms of apparent lattice deformation and defect mechanisms.

CE-1:L14 Ultra-high Temperature Ceramics Containing TaSi2: Production, Microstructure Characterization, Mechanical and Oxidation Properties

Laura Silvestroni*, Diletta Sciti, CNR-ISTEC, Institute of Science and Technology for Ceramics, Faenza, Italy

ZrB2 and HfB2 possess a unique combination of properties, such as high melting point, high hardness and strength, good oxidation resistance and high thermal conductivity, which make them potential candidates for components in future hypersonic vehicles.In this work, TaSi2 was added to Zr and Hf borides to promote the densification and improve the oxidation resistance.The microstructure of the hot pressed composites was analyzed by X-ray diffraction, scanning and transmission electron microscopy to investigate the densification mechanisms. The formation of (Ta,Me)B2 solid solution surrounding the matrix was observed in both ceramics. The analysis of secondary phases, triple points and grain boundary confirm the densification is helped by liquid phase. Vickers hardenss, fracture toughness, elastic modulus, 4-pt bending strength in air up to 1500 °C were evaluated. HfB2-based ceramic exhibited the best properties and the strength at 1500 °C was still 600 MPa. Oxidation tests were carried out at 1600 °C in air to assess the effectiveness of TaSi2 as protective phase. Finally, arc-jet experiments in high enthalpy hypersonic flow were carried out on the HfB2-based composite to evaluate the aerothermal behaviour on two models with hemispher and cone-shaped geometry.

CE-1:L15 Oxidation Behaviour of HfB2 Based Ceramics at Intermediate (~1600 °C) and Ultra High (~3000 °C) Temperatures

D.D. Jayaseelan[1]*, P. Brown[2], W.E. Lee[1], [1]Structural Ceramics Centre, Dept. of Materials, Imperial College London, UK; [2]Dstl, Porton Down, Salisbury, Wiltshire, UK

As part of a UK government programme looking at materials for future hypersonic vehicle leading edge applications spark plasma sintering has been used to fabricate 40mm diameter, 6mm thick samples of HfB2/20 vol. % SiC. Oxidation studies were performed in air at two different conditions: (i) 1600 °C for 1 h to 5 h in a small laboratory furnace and (ii) in excess of 3000 °C for 30 sec to 120 sec using a 10mm diameter defocused laser (DFL) beam. After exposure for 5 h at 1600 °C no significant change in the mass or surface oxidation layer thickness of samples was observed. In addition to hafnia and silica, phase analysis of oxidised surfaces also detected in-situ formed hafnates and oxycarbides. Owing to their low oxygen permeability these phases were considered to have a beneficial effect on the oxidation resistance of HfB2/20vol.% SiC at intermediate temperatures. The oxidised surface of samples subjected to DFL testing had the appearance of a porous crust although samples retained a high degree of dimensional and physical integrity. Unique oxidation features were also observed and characterized using X-ray diffraction, scanning electron microscopy, focussed ion-beam and transmission electron microscopy.

CE-1:L16 Titanium Carbide Reinforced Composite Ceramic Tools Based on Alumina

Szutkowska Magdalena[1]*, Smuk Barbara[1], Boniecki Marek[2], [1]The Institute of Advanced Manufacturing Technology, Cracow, Poland; [2]The Institute of Electronic Materials Technology, Warsaw, Poland

Recent advances in high-speed cutting materials have focused on reinforcing alumina with different carbides, oxides and nitrides in order to improve hardness, fracture toughness and wear resistance. The potential use of this type of material for cutting tool applications has yet to be determined. The present study reports some preliminary results obtained by reinforcing Al2O3-10 wt.% ZrO2 (partially stabilized with Y2O3 -Y5) composite with TiC in amount of 5 wt.%. Specimens were prepared on the basis submicro and nano scale trade powders. The material was cold-pressed at 250 MPa. The specimens were sintered in a vacuum high temperature furnace type Balzers at 1700°C with various sintering times from 60 to 180 min and then characterized. Vicker's microhardness (HV), Vicker's hardness (HV30), apparent density and absorbability by the hydrostatic methods, fracture toughness (KIC) at room and high temperature characteristic for tool work were evaluated. Wear resistance (Vn) very important property for tool ceramics was specified by the speed of mass lost. The observationof the microstructure of specimens, thermally etched in vacuum , was carried out using scanning electron microscopy (SEM). For comparison, ceramics Al2O3 with 20 wt.% ZrO2 (ZY5) was accepted. The addition of TiC nano powder results in significant improve of fracture toughness up to 5 MPam1/2 at the hardness increase to 20 GPa. Preliminary industrial tests confirm the high cutting performance of tested alumina composite cutting inserts.

CE-1:IL17 Factors Affecting Oxidation Kinetics of Refractory Diborides

T.A. Parthasarathy*, R.A. Rapp**, M. Opeka***, M.K. Cinibulk, Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/RXLN, Wright-Patterson AFB, OH, USA; *UES, Inc., Dayton, OH, USA; **The Ohio State University, Columbus, OH, USA; ***Naval Surface Warfare Center, Carderock, MD, USA

The need for ultrahigh temperature oxidation resistance in future aircraft designs has resulted in a search for optimal compositions of Ultra High Temperature Ceramics (UHTC). Designing with these novel compounds for use in an aggressive environment with gradients in imposed service conditions, requires an understanding of the various factors that affect the kinetics of recession and oxidation product development. Towards this need, and to help predict possible compositions that might enhance the oxidation resistance further, we have developed a mechanistic model that interprets the various unique aspects of the oxidation kinetics of zirconium and hafnium diborides. Available thermodynamic data and literature data for vapor pressures, oxygen permeability in boria, and viscosity of boria were used to evaluate the model. Transitions in oxidation mechanisms with temperature are shown to be important in rationalizing experimental data. Good correspondence was obtained between theory and experiments for weight gain, recession, and scale thickness as functions of temperature and oxygen partial pressure. We use the model to identify key factors that govern the oxidation behavior of UHTC materials, and suggest possible methods to improve the oxidation resistance further.

CE-1:IL18 Novel Non-contact Measurement of Creep in ZrB2 and ZrB2-SiC Composites

R.W. Hyers*, University of Massachusetts, Amherst, MA, USA; J.R. Rogers, NASA Marshall Space Flight Center, USA

A novel approach to measuring creep at extremely high temperatures using electrostatic levitation (ESL) has been developed. This method has been demonstrated on niobium up to 2300 °C, while ESL has melted tungsten (3400 °C). High-precision machined spheres of the sample are levitated in the NASA MSFC ESL, a national user facility, and heated with a laser. The sample is rotated at speeds exceeding 500,000 revolutions per minute using an induction motor. The rapid rotation loads the sample through centripetal acceleration, causing it to deform. The deformation of the sample is captured on high-speed video, which is analyzed by machine-vision software from the University of Massachusetts. The deformations are compared to finite element models to determine the constitutive constants in the creep relation. Furthermore, the non-contact method exploits stress gradients within the sample to determine the stress exponent in a single test. This method was validated against conventional tensile creep measurements for niobium at 1985 °C. Now this method is being employed to measure creep in Ultra-High-Temperature ZrB2- SiC composites. A detailed overview of the method will be presented along with the latest results.

Session CE-2
Nitride, Carbide and Boride Ceramics

CE-2:IL01 Development of Nano-sized TiN Dispersed Si3N4 Ceramics

K. Komeya*, J. Tatami, T. Wakihara, T. Yamakawa, Yokohama National University, Yokohama, Japan

Si_3N_4 is one of the most attractive materials for the bearing applications because it has excellent wear resistance and offers advantages such as light weight, higher strength and toughness, and good corrosion resistance. Subsequently it was confirmed that the addition of TiO_2 and AlN to an Si_3N_4-Y_2O_3-Al_2O_3 system promoted densification at low temperatures. During firing, the TiO_2 changed into TiN at the grain boundary, causing grain boundary strengthening. Recently we have developed a new Si_3N_4 ceramics designed with nano-sized TiN dispersion in the grain boundary, which shows lower damage for mating material in the bearing system. The purpose of this work is to promote the newly innovated Si_3N_4 ceramics seeds to the highly reliable bearing balls toward the high end applications. The key processing factor is to design and control nano-dispersion of TiN in the sintered bodies. To achieve homogeneous dispersion, we used several powder mixing techniques, especially mechano-chemical bonding method to fabricate composite particles. In this research, parameters such as contents of nano-particles and mixing, molding and firing conditions were examined. The outlines of research items and the activities carried out are presented in this paper.

CE-2:IL02 Phase Equilibria in B4C-based Ceramics

H.J. Seifert, Technical University of Freiberg, Institute of Materials Science, Freiberg, Germany

The current knowledge on phase equilibria in B4C-based ceramic systems will be discussed in context with thermodynamic data and solution phase modelling. An overview on the binary boron-carbon phase diagram and the thermodynamic calculations in this system will be given. The homogeneity range of the boron carbide phase was described by using a sublattice model and taking into account the occupation of crystallographic sites with various structural species. Recently, numerous ternary B-C based systems including the boron carbide phase (B4+xC) were critically assessed. Many of these systems are of interest for the pressureless sintering of boron carbide. An overview will be given and selected systems will be discussed in more detail such as B-C with N, Si, Al, Cr and other elements, respectively. Individual phase diagram topologies in isothermal sections and isopleths and their consequences for the sintering of B4C-based ceramics will be outlined. So far, only few B-C-based multicomponent multiphase systems were thermodynamically modelled. As an example for the use of such modelling, computer calculations in the Si-B-C-N system including the boron carbide phase will be introduced.

CE-2:IL03 Defect Detection in Ceramic Armor Using Phased Array Ultrasound

William A. Ellingson*, Argonne National Laboratory, Argonne, IL, USA; J. Scott Steckenrider, Illinois College, Jacksonville, IL, USA; Thomas J. Meitzler, US Army, Warren, MI, USA

Monolithic SiC ceramic tile is often used as part of ceramic-composite armor. Rejection of individual tile that contain potential threat-defeat-reducing “defects” must be accomplished in a fast and cost-effective manner. Water-immersion phased-array ultrasound using 10 MHz 128-element transducers sequenced at 32-elements has been demonstrated to quickly scan and detect 25-50 um known inclusion-type defects in individual 25 mm thick SiC tile. Further, use of similar phased-array transducers and similar transducer-element activation sequences, has shown detection of intentional internal defects in tests of 40 cm square by 50 mm thick, multi-layered ceramic composite armor specimens. Large changes in acoustic velocities of the various layered materials causes focusing issues of the ultrasonic wave. The use of various digital signal processing method can be used to overcome some of these issues. The results show that use of phased array ultrasound can reliably be used for defect detection in either monolithic or composite ceramic armor. The technology and various results are presented.

CE-2:IL04 Silicon Nitride Ceramics - Microstructural Tailoring and Mechanical Properties

M.J. Hoffmann*, S. Fünfschilling, Th. Fett, Karlsruhe Institute for Technology, Institute for Ceramics in Mechanical Engineering, Karlsruhe, Germany

Silicon nitride ceramics are used in numerous applications as high-temperature structural components, cutting tools or wear parts. The materials are densified by liquid phase sintering using oxide additives to obtain a multiphase microstructure with elongated silicon nitride grains surrounded by an amorphous or partially crystalline grain boundary phase. The first part of the presentation describes briefly the impact of different rare earth (RE) additives on the growth anisotropy of silicon nitride crystals. It will be shown that growth anisotropy is controlled by the adsorption behaviour of RE cations at the interface between grains and intergranular films. Based on the fundamental growth parameters, samples had been prepared with various additives showing a similar microstructure, but different interfacial bonding. The mechanical behaviour of the different compositions has been subsequently characterized by measuring R-curve behaviour and strength. It will be demonstrate that the R-curves start at about 2MPam$^{1/2}$ for all compositions and reach nearly saturation within a few µm. The plateau values for the materials are in the range of 5.5 MPam$^{1/2}$ to 7.2 MPam$^{1/2}$. In order to measure the increase of the R- curve in the early stage, we developed a modified compliance method and take into account that the stress intensity factors for cracks developing in front of notches are clearly smaller than formally computed from the “long-crack solution”. Crack tip toughness was determined from COD measurements. Finally the bridging stress distribution was determined from the R-curve. For this calculation no bridging law was specified and therefore the distribution of the stresses was not effected by the any assumption. The maximum values of the bridging stresses are in the range of -1200 to -1700 MPa depending on composition. Using this data we estimate the maximum obtainable strength for a silicon nitride ceramic.

CE-2:L05 Microstructure and Mechanical Properties of Rare-earth Doped Si3N4 and Si3N4/SiC Ceramics

P. Tatarko[1], S. Lojanová[2], Z. Chlup[3], J. Dusza[1]*, P. Sajgalík[2], [1]Institute of Materials Research, SAS, Kosice, Slovak Republic; [2]Institute of Inorganic Chemistry, SAS, Bratislava, Slovak Republic; [3]Institute of Physics of Materiále, Academy of Sciences of the Czech Republic, Brno, Czech Republic

The influence of rare-earth oxide additives (La2O3, Y2O3, Yb2O3 and Lu2O3) on the microstructure and mechanical properties of hot-pressed silicon nitride and Si3N4 + SiC nanocomposites have been investigated. The composites exhibited finer microstructure compared to monolithic materials and the aspect ratio of the Si3N4 grains increased with decreasing ionic radius of rare-earth elements both in monolithic Si3N4 and in Si3N4+SiC nanocomposites. Chevron Notched Beam technique and four-point bending mode have been used for fracture toughness and strength measurements, respectively. The hardness of both kinds of material increased with decreasing ionic radius of rare-earth element. The fracture toughness of monoliths was higher due to the coarser microstructures and due to more toughening mechanisms during the crack propagation. Materials with higher aspect ratio of the Si3N4 grains (Lu or Yb additives) exhibited crack deflection more frequently compared to the Si3N4 doped with La or Y, which was responsible for the higher fracture toughness. The bending strength slightly increased with decreasing ionic radius of rare-earth element. The positive influence of finer microstructure of the composites on the strength was not observed because of the present strength degrading defects.

CE-2:L06 Tribo-mechanical Properties of Carbon Nanotubes/Silicon Nitride Nanocomposites

J. Gonzalez-Julian[1], J. Schneider[2], P. Miranzo[1], M.I. Osendi[1], M. Belmonte[1]*, [1]Institute of Ceramics and Glass (CSIC), Campus de Cantoblanco, Madrid, Spain; [2]Akademischer Oberrat, Universität Karlsruhe (TH), Institut für Werkstoffkunde II c/o Forschungszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany

Due to the outstanding thermo-mechanical and electrical properties of carbon nanotubes (CNTs), their additions to different ceramic matrices have been intended to enhance composite properties. Silicon nitride (Si3N4) ceramics are a family of high temperature materials used in structural applications, which can be potentially upgraded by the addition of CNTs. The aim of this work was to study the tribological and mechanical properties of CNTs/Si3N4 nanocomposites. Proprietary method was used to get fully dense nanocomposites with CNTs contents up to 8.6 vol%, having a good dispersion of the nanotubes in the matrix while avoiding their degradation. For that, spark plasma sintering technique was required. The tribological measurements were carried out in reciprocating self-mated ball-on-flat tribotester under isooctane lubrication and severe loaded contacts. The nanocomposites presented an excellent tribological performance, decreasing the friction coefficient and the linear wear in 45% and 84%, respectively, compared to the monolithic material. The mechanical properties, determined by indentation methods, strongly depended on the amount of CNTs and the nanotube/Si3N4 interface, which was enhanced through CNTs functionalization.

CE-2:L07 Hot Pressed SiC-AlN Materials System - Solid Solution Effects

Biljana Mikijelj[1]*, Zubair Nawaz[1], Jane Adams[2], Jerry LaSalvia[2], [1]Ceradyne Inc, Costa Mesa CA, USA; [2]ARL, Aberdeen proving grounds, Aberdeen, MD, USA

Effects of compositions, starting powders and processing temperatures on solid solution formation and microstructure were investigated in the SiC-AlN system. The present work aims to evaluate the progress of solid solution formation effects on hardness, toughness and strength of SiC-AlN materials via hot pressing above the δ(ss) formation temperature. The solid solution separation effects on material properties will be evaluated after heat treating and verification by TEM. Some of materials in this system will be evaluated as potential armor materials.

CE-2:IL08 Development of Scanning Microwave Technology for Ceramics in Extreme Environments

Jack R. Little, Jr., Evisive, Inc., Baton Rouge, Louisiana, USA

Advanced ceramic materials are required to meet increasing high temperature demands of components in advanced propulsion engines for high performance aircraft as well as increasing structural demands in ceramic-composite armor. Monitoring the structural performance of these advanced ceramic materials presents challenges. Recently a new technology, Evisive ScanTM, based on microwave interferometry has been developed that allows condition monitoring. The internationally patented Evisive ScanT method utilizes microwaves to interrogate dielectric materials. The microwaves are reflected at areas of changing dielectric constant. The reflected energy and the interrogating beam are combined to form an interference pattern which is measured in the transceiver as a signal voltage. The signal voltage is sampled at many positions in the inspection area. This point cloud is displayed as an Evisive ScanT image, which presents volumetric detail of the inspected part. Over the past two years the technology has been demonstrated on Ceramic Matrix Composites and has shown to be an efficient measurement of porosity and manufacturing defects. The method has also been demonstrated to be applicable to ceramic composite armor made of monolithic ceramic tiles in complex, multilayer structures. This paper will describe the technology and provide examples of results.

CE-2:L10 Ceramic Tool Materials for High Speed Cutting Process

Gabriela Górny, Roman Pampuch*, Ludos³aw Sobierski, Marian Raczka, Faculty of Materials Science and Ceramics, University of Science and Technology, Krakow, Poland

The present study concentrates on sintering and mechanical properties of a new Si$_3$N$_4$ - matrix composite reinforced with h-BN as a solid lubricant, possesses good comprehensive mechanical properties. Using XRD-phase analysis, computer-aided analysis of microstructure and stepwise regression analysis relationships havee been derived between fracture toughness and material composition in order to estimate the optimum range of volume fractions of h-BN.. The work has been supported by EU Funds in Poland under contract UDA-POIG.01.03-12-024/08-00. and has been realized by a scientific-industrial consortium.

CE-2:L11 Synthesis of Needle-like TiN Particles and their Application to TiN-Si3N4 Composite

H. Kiyono*, Y. Nihei, Y. Miyake, S. Shimada, Hokkaido University, Sapporo, Japan; T. Tsumura, Oita University, Oita, Japan

Titanium nitride (TiN) is a promising material for coatings of cutting tools and additive in composites. TiN-Si3N4 composites have been fabricated to improve electrival conductivity or fracture toughness. In these studies, size of TiN particle was controlled but shape has not been controlled. In the present study, needle-like TiN particles were synthesized by nitridation of TiO2 nano-fiber and were applied to Si3N4 based composites. TiO2 nano-fiber was synthesized by hydrothermal treatment of TiO2 powder. The synthesized TiO2 nano-fiber was transformed to TiN by heating in NH3. Composite of Si3N4-15 vol% TiN was fabricated by hot-pressing at 1850 °C for 1 h in N2. Needle-like TiN particles of 5-10 micro-m length was successfully synthesized by heating at 1000 °C. Hot-pressed composite was densified up to 97% relative density. The composite consists of alfa-Si3N4 and TiN with a small amount of beta-Si3N4. Fracture strength and hardness of the composite were 5-9 MPa•m1/2 and 17-22 GPa, respectively.

CE-2:L12 Boron Suboxide - based Composites: Thermal Stability and Tribological Testing

I. Sigalas*, C. Freemantle, University of Witwatersrand, Johannesburg, Wits, South Africa; M. Herrmann, Fraunhofer Institute of Ceramic Technologies and Systems, Dresden, Germany

Boron suboxide based composites have been found to possess hardness and fracture toughness similar to those of PCBN cutting tool materials. In this work we report thermal stability, diffusion couple, as well as testing in machining of B6O-Al2O3/Y2O3 composites. Static interaction diffusion couple experiments, involving B6O and Compacted Graphite Iron, showed that Interactions below 900 °C were minimal, with significant chemical interactions occurring at 1100 °C and above. Iron boride phases were seen to evolve at the interface of the tool and workpiece materials. Silicon diffusion has been identified as a rapidly diffusing constituent with a tendency to diffuse towards the interface. The chemical products generated during the experiments indicate that chemical wear will affect B6O tools at machining temperatures. Resistance to oxidation of B6O based materials was examined at 1000 °C, revealing a tendency for formation of boric acids on the surface of the material, caused by B2O3 formation and reaction with atmospheric moisture. Turning tests have revealed that B6O based cutting tools perform comparably with PcBN at low cutting speeds, but suffer abrasive wear as the cutting speed is increased. Improvement in cutting edge preparation has shown marked improvement in performance.

CE-2:IL13 Microstructural Design of Si3N4 Ceramics via Preceramic Polymer Additives

G. Motz, University of Bayreuth, Bayreuth, Germany

Preceramic polymers were developed especially for processing of ceramic fibers, polymer and ceramic coatings as well as for matrix material for e.g. CMCs. Due to their versatile shaping and the conversion into ceramics at elevated temperatures preceramic polymers offer a great potential for the use as binders for ceramic powders. An appropriate technology on the basis of specially tailored SiCN polymers as the ceramic forming binder and Si3N4 powder was developed. At first the ceramic particles were coated with the polymer by different granulation processes. Subsequent compression molding and crosslinking at 300 °C leads to very good machinable bodies. Pyrolysis at 1000 °C results in porous ceramics with good thermal stability by reduced mechanical strength. But also nearly theoretically dense high performance Si3N4 ceramics with a homogeneously distributed nano scaled SiC phase resulting from the carbon content of the used SiCN precursor are feasible by subsequent sintering at approx. 1800 °C. By varying the ceramic powder and the preceramic binder the developed powder-binder technique is suitable for manufacturing different ceramic materials with adjustable structures. It offers also a great potential to produce different composite materials cost effectively in a large scale.

CE-2:IL14 Robust Net Shape Forming of High Temperature Silicon Nitride Based Gas Turbine Components

Vimal K. Pujari*, Ara Vartabedian, Gregg Wayman, Saint-Gobain Ceramics & Plastics Inc., Northboro, MA, USA

A reliable and environmentally friendly aqueous closed loop processing method for a high temperature silicon nitride material (NT154) and associated technique for its near net shape forming methodlogy will be described. High temperature fast fracture, oxidation and time dependent (Slow Crack Growth) properties relevant to gas turbine application will be highlighted. Utilizing this material an advanced CNC green machining based complex shape forming technology will be described which has been shown to be robust with reproducibility, high yield and capable of rapid prototyping.Fully dense NT154 Integral Bladed Rotors (IBR) and Rings for small gas turbine applications have been fabricated with dimensional controls within 0.15% and as process surface roughness of less than 1 micron. Finished components have been successfully tested at 120% of the design stresses without failure. This test data from fully machined component has been utilized to further optimize the dense machining procedure. Following this approach, a cost effective manufacturing base has been established to provide prototype gas turbine grade componenets to OEMs for rig and engine testing for future civilian and military applications such as APUs, Microturbines, UAVs etc.

CE-2:L15 SiC Nanostructured Ceramics from Laser Grown Nano-powders Sintered by SPS

Y. Leconte*, X. Landreau, S. Coste-Leconte, N. Herlin-Boime, CEA, IRAMIS, SPAM, LFP, Gif sur Yvette, France; G. Bonnefont, G. Fantozzi, MATEIS, UMR CNRS 5510, Université de Lyon, INSA de Lyon, Villeurbanne, France

Carbide ceramics as SiC are potential candidates for high temperature applications such as fourth generation nuclear plants because of their refractory properties and their low activation under neutron irradiation. Nevertheless, their typical brittleness could limit their use in these applications. In this context, decreasing the grain size down to the nanometric scale could enhance the mechanical properties such as strength and/or toughness, whether these ceramics are used as bulk materials or as matrix in composites. The first challenge that has to be faced is the elaboration of the nanostructured ceramics samples, which means being able to synthesize the pre-ceramics nanopowders in weighable amounts and then finding an efficient way to sinter them aiming at the maximum densification together with avoiding grain growth. In this contribution, we present SiC nanopowders synthesis by laser pyrolysis together with their densification by Spark Plasma Sintering (SPS). Gaseous precursors (SiH4, C2H2) were used for SiC nano-powders synthesis by laser pyrolysis. The powders were pressed without sintering additives, and the SPS pressure was fixed to 75 MPa. SPS temperature, holding time and moment of pressure application were varied in order to observe the effects on the densification and the grain growth. The influence of the green body preparation is also reported together with Vickers hardness measurements.

CE-2:L16 The Effects of C and SiC for Sintering Si3N4/SiC Composites

C. Sahin[1]*, Z. Taslicukur[1], F. Cinar Sahin[2], N. Kuskonmaz[1], [1]Yildiz Technical University, Metallurgical and Materials Engineering Department, Istanbul, Turkey; [2]Istanbul Technical University, Metallurgical and Materials Engineering Department, Istanbul, Turkey

In this study, the effects of C and SiC for sintering Si3N4/SiC composites, were investigated. The experiments were carried out begining from same raw material mixtures but the percentage of C black was changed.

Y2O3, AlN were used as sintering additives. Also mixtures with direct SiC were also prepared to compare with the carbon black added mixtures. The powders were cold isostatically pressed. The effects of carbon black percentage in the mixtures were analysed by characterization of SiC particles which were obtained in the Si3N4 matrix. Sintering temperature, time and all the effects on in-situ reaction were studied.

CE-2:IL17 **Hot Rolling Steels and Super Alloys with Silicon Nitride Tools**

Robert Danzer, Institut für Struktur- und Funktionskeramik, Montanuniversität Leoben, Leoben Austria

Tools for rolling steels and super alloys, which are nowadays made in general from steel or cemented carbides, suffer for wear and/or for surface cracking due to thermal fatigue. Due to their high strength, hardness and thermal shock resistance it can be expected that silicon nitride rolls have an improved behaviour. But their low toughness causes also a high risk of brittle failure, if the loading is not accurately taken into account by a proper design. In this contribution examples for the successful use and for failing of silicon nitride rolls are given. On the example of heavy loaded rolls for wire rolling the behaviour of small surface cracks in the roll track are discussed. It is shown that - for the investigated conditions - rolling high strength steel wires is manageable but rolling of super alloy wires will cause the growth of fatigue cracks, which may destroy the rolls after some tons of rolled wire. Relevant aspects for proper design are discussed and critical situations are outlined.

CE-2:IL18 **Silicon Nitride Ceramics for Product and Process Innovation**

Karl Berroth, FCT Ingenieurkeramik GmbH, Rauenstein, Germany

During the last years large efforts were made, to get able to supply large and complex components made of gas pressure sintered silicon nitride. This opened new applications for such ceramic materials in ambient and very harsh environment and generated new markets for ceramic producers. The paper presents, a newly developed rapid prototyping routine for complex components as well as the properties of corresponding materials. Components for innovative avionic and space applications, dynamic materials testing, liquid metal processing, metal forming and mechanical engineering are shown. Not only unique properties of the material itself, but also newly developed and adopted shaping and machining technologies for this specific ceramics have let to highly valued products. Due to its very specific set of material properties, silicon nitride has gained a lot of interest. New approaches in technical equipment were undertaken with corresponding research. However, except of seals, bearings and cutting tools, none of all expected high volume applications is industrialized. On the other side, a lot of less spectacular applications are state of the art today. They have opened a wide field for niche products and lead to technical solutions with less wear and corrosion but improved products.

CE-2:L19 **Electrical Discharge Machining of B4C-TiB2 Composites**

Olivier Malek[1, 2]*, Jef Vleugels[2], Shuigen Huang[2], Yeczain Perez[3], Patrick de Baets[3], Bert Lauwers[1], [1]K.U. Leuven, Dept. of Mechanical Eng., Leuven, Belgium; [2]K.U. Leuven, Dept. of Metallurgy and Materials Eng., Leuven, Belgium; [3]Universiteit Gent, Mechanical Construction and Production - Laboratory Soete, Gent, Belgium

The interrelationships between the material properties and the electrical discharge machining (EDM) behaviour of B4C-TiB2 composites with respectively 30, 40 and 60 vol. % TiB2 are investigated. The composites were fully densified by means of Pulsed Electric Current Sintering (PECS). Special attention was given to the influence of the grain size on the EDM behaviour by producing composites with a nanometric TiB2 phase using in-situ synthesis during PECS. As reference material, a commercially available hot pressed B4C-TiB2 composite with 40 vol. % of TiB2 was used. The experimental work revealed that 40 vol. % of TiB2 results in an optimal Material Removal Rate (MRR) while the surface roughness (Ra) for the rough cut EDM decreases with increasing TiB2 content. The finer microstructure of the nanometric in-situ synthesized composite shows higher MRR's and lower Ra values than the commercial powder based composites. The major material removal mechanism (MRM) for the PECS based composites was melting whereas spalling or thermal shock was observed for the commercial hot pressed composite. This difference is due to the presence of free carbon at the grain boundaries in the commercial material, providing a weaker grain boundary interface compared to the PECS B4C-TiB2 interfaces.

Session CE-3

Precursor Derived Ceramics

CE-3:IL01 **New Precursors for Synthesis of High Temperature Ceramics**

Caihong Xu, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

A series of new precursors for synthesis of high temperature non-oxide ceramics have been developed. By choice of chlorosilanes or adjustment of their ratios, the precursors for Si-C-N based ceramic, polysilazanes, which have different compositions and processing properties were achieved by simple co-ammonolysis reactions. With 1,3,5-trichloroborazine as starting material, molecules containing cyclic structure units and/or reactive functional groups were prepared and used as precursors for BCN, BN, SiBCN, and SiBC ceramics.

CE-3:IL02 **Characterization of Polymer-Derived Ceramics via Transmission Electron Microscopy**

Hans-Joachim Kleebe, Technische Universität Darmstadt, Institute for Applied Geosciences, GeoMaterial Science, Darmstadt, Germany

One of the interesting issues in PDCs is the question of the role of excess carbon. Transmission electron microscopy studies on carbon-rich SiOC focused on the nano-domain size evolution with increasing temperature. The high carbon content in the PHMS based polymer-derived ceramic was achieved by utilizing DVB as an intrinsic crosslinking agent. The generation of carbon- and silica-rich regions within the amorphous matrix raises the questions of domain size and their thermal stability. The role of carbon with respect to phase separation and corresponding evolution of carbon- and silica-rich nano-domains, which in turn favor a unique viscoelastic response, will be presented. Recent investigations focus on the microstructural evolution of a SiOC ceramic, modified by hafnium(IV)n-butoxide. These materials were characterized with respect to the formation of HfO2 precipitates within the amorphous silicon oxycarbide host matrix. Emphasis here was to verify as to whether the samples revealed a homogeneous distribution of the hafnia particles within the matrix. Local inhomogeneities of both precipitate size and dispersion were observed, which will be discussed in the context of thermal stability (decomposition) and/or local variations in diffusivity within the amorphous host matrix.

CE-3:L03 **Development of Zirconia-toughened Mullite Matrix Composites from a Nano-filled Preceramic Polymer**

E. Bernardo, G. Parcianello*, P. Colombo, University of Padova, Padova, Italy

Mullite is well known to possess outstanding physical properties, such as low density, low thermal conductivity, low thermal expansion, low dielectric constant, and excellent creep and thermal shock resistance. The limit for extensive structural application of mullite ceramics is represented by the relatively low fracture toughness (<3 MPa $m^{0.5}$), which can be much improved by preparing mullite matrix composites. A novel synthesis method, based on the dispersion of γ-Al2O3 nanoparticles in a solution of silicone resin, has been recently proposed for the production of high-purity mullite. In the present work we extended the "nano-filling approach" to the preparation of zirconia-toughened mullite, by inserting ZrO2 nanoparticles in addition to γ-Al2O3 nanoparticles. This method was effective in yielding tetragonal ZrO2 nanocrystals embedded in mullite, capable of stress-induced transformation (martensitic tetragonal-monoclinic ZrO2 transformation) during propagation of cracks into the matrix and thus leading to much tougher composites than un-reinforced mullite. Preliminary results showed an almost three-fold increase of fracture toughness,from 2.1 MPa $m^{0.5}$, for unreinforced mullite, to the value of 5.8 MPa $m^{0.5}$, for mullite reinforced with 20 vol% ZrO2.

CE-3:L04 **High-temperature Behavior of Novel SiOC/HfO2 Ceramic Nano-composites at T>>1000 °C**

B. Papendorf*, E. Ionescu, R. Riedel, Institut für Materialwissenschaft, Technische Universität Darmstadt, Darmstadt, Germany; H.J. Kleebe, K. Nonnenmacher, Institut für Geowissenschaft, Technische Universität Darmstadt, Darmstadt, Germany

In the present work, hafnia-modified SiOC-based polymer-derived ceramic nanocomposites have been synthesized and evaluated with respect to their high temperature stability at T >> 1000 °C. The synthesis of the materials was performed via cross-linking and ceramization of a commercially available polysiloxane (Wacker Belsil® PDMS MK polymer), which has been chemically modified by hafnium alkoxide. The influence of the hafnium alkoxide on the thermal stability and microstructure evolution of SiOC/HfO2 ceramics at temperatures up to 1600 °C was studied. XRD and electron microscopy (SEM, TEM) investigations showed the formation of hafnon nanoparticles within the SiOC matrix at temperatures beyond 1450 °C. This process can be seen as a solid-state reaction of silica with hafnia and should be considered as a concurrent reaction to the carbothermal decomposition of SiOC. Thus hafnia modification of SiOC remarkably improves the thermal stability thereof with respect to decomposition. Annealing of SiOC/HfO2 ceramic materials at T > 1450 °C leads to hafnon-based nanocomposites. Their thermal stability in argon and air atmosphere was investigated and will be discussed.

The authors thank the German Science Foundation (DFG) for financial support (SPP 1181).

Session CE-4
Ternary Compounds

CE-4:IL01 **The Max Phases: Ductile, Machinable Ternary Carbides and Nitrides for High Temperature and Other Applications**

Michel W. Barsoum, Department of Materials Science and Engineering Drexel University, Philadelphia, PA, USA

The layered, hexagonal carbides and nitrides with the general formula: Mn+1AXn, where n = 1 to 3, M is an early transition metal, A is an A-group (mostly IIIA and IVA) element and X is either C and/or N - sometimes referred to polycrystalline nanocomposites since every basal plane is a potential deformation or delamination plane - combine some of the best attributes of metals and ceramics. Like metals, they are electrically and thermally conductive, most readily machinable, not susceptible to thermal shock, plastic at high temperatures, and exceptionally damage tolerant. Like ceramics, they are elastically rigid, lightweight, and maintain their strengths to high temperatures. The ternaries Ti3SiC2 and Ti2AlC are creep, fatigue and oxidation resistant. More recently we have also shown that the MAX phases are but a subset of solids that we termed kinking nonlinear elastic, KNE, because one of their important - and in many cases only - deformation mode is the formation of fully reversible, dislocation-based incipient kink bands, IKBs. Exploiting this phenomenon, we engineered Mg/Ti2AlC composites that combine record damping (0.6 MJ/m3), strengths and ease of machinability with effective moduli of the order of 70 GPa. The implications of these results and others will be discussed.

CE-4:IL02 **Low Cost Processing and Property Control of Layered Ternary Carbides and Nitrides (MAX Phases)**

Yanchun Zhou, High-performance Ceramic Division, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

The layered ternary compounds Mn+1AXn, where M is a transition metal, A is an IIIA or IVA element, X is C or N, combine the merits of both metals and ceramics. The salient properties of this family of materials include low density, high strength and modulus, damage tolerance at room temperature, good machinability, and being resistant to thermal shock and oxidation. The unique combination of these properties make them possible for applications in aerospace industry, GIV nuclear reactors, solid oxide fuel cell, metallurgy, etc., as either structural components or as corrosion resistant coatings. However, the high fabrication cost, rapid decrease of strength at high temperatures, decomposition at high temperatures in vacuum or reaction with environmental gases limit their widespread applications. To overcome these application obstacles, low cost methods to make large size and complex shape samples must be developed. In this talk, methods to reduce the fabrication cost such as pressureless sintering, electrophoretic deposition (EPD) and reaction/diffusion bonding to make large size components will be introduced. And novel routes such as solid solution strengthening, particulate strengthening with SiC, TiC, ZrC, TiB2 and Al2O3 phases, formation of protective layers at high temperatures to improve the properties will be discussed.

CE-4:L03 **Thermal Stability of Ti3Al1-xSixC2 Solid Solutions**

Jixin Chen*, Y.C. Zhou, J. Zhang, SYNL, Institute of Metal Research, CAS, Shenyang, China

An abnormal expansion was found in the Ti3Al1-xSixC2 solid solutions during the first-time heating. There is an inflexion during heating for the solid solutions but this phenomenon is absent during cooling and re-testing, which results in a residual specific elongation of 460-1800 ppm. This was ascribed to the volume expansion caused by the precipitation of Ti5Si3 phase and the formation of the solid solutions with lower Si content. The starting precipitation temperature of Ti5Si3 was determined as 940 °C, which was also confirmed by the results of high-temperature Young's modulus. There was a mechanical damping peak at around 940 °C. However, the precipitation of Ti5Si3 slows down at temperatures above 1100 °C. TEM study showed that Ti5Si3 phase usually precipitated on the grain boundaries of Ti3Al1-xSixC2 solid solutions.

CE-4:L04 **Thermal Stability of MAX Phases in Vacuum**

W.K. Pang, I.M. Low*, Dept. of Applied Physics, Curtin University of Technology, Perth, WA, Australia

The thermal stability MAX phases (Ti2AlC, Ti2AlN, Ti3AlC2, and Ti4AlN3) to high-temperature thermal dissociation in vacuum has been investigated using in-situ neutron diffraction. In high vacuum, these phases decomposed above 1400 °C through the sublimation of M and A elements, forming a surface coating of MX. An Arhenius equation was used to determine the apparent activation energies for the decomposition of these phases. The spontaneous release of a lower-order 211 phase from the de-intercalation during decomposition of 312 and 413 phases resulted in a negative activation energy.

CE-4:L05 **Pressureless Sintering and Properties of Ti3AlC2**

X.P. Lu*, Y.C. Zhou, High-performance Ceramic Division, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

The layered ternary carbide Ti3AlC2 exhibits unique combination of merits of both metals and ceramics. These salient properties include low density, high strength and modulus, good electrical and thermal conductivity, and good resistance to thermal shock and high temperature oxidation. Traditionally, hot-pressing (HP), hot isostatic pressing (HIP), and pulse discharge sintering (PDS) are used to prepare dense Ti3AlC2. In all of methods mentioned above, pressure is needed to densify the Ti3AlC2 compacts, which limits the size and shape of parts that can be produced. Pressureless sintering has the advantage of preparing samples with complex shape and large size, which is of significance for promoting ceramics to be used in industry. Pressureless sintering of Ti3AlC2 is difficult due to its easy decomposition at high temperatures. In this work, pressureless sintering was performed in Al4C3 embedded powders, which can effectively inhibit Ti3AlC2 from decomposition by offering an Al rich ambience. High density Ti3AlC2 was obtained without additives, and the densification is due to the special structure of Ti3AlC2 and the easy diffusion of Al element. The mechanical properties (Vickers hardness, flexural and compressive strengths, fracture toughness, elastic modulus, and damping property) of pressureless sintered Ti3AlC2 were systematically characterized.

CE-4:IL06 **Structure and Property Control of Layered Ternary Carbides and Nitrides**

Jingyang Wang*, Yanchun Zhou, High-performance Ceramics Division, Shenyang National Laboratory for Materials Research, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

High-temperature binary transition-metal carbides and nitrides are typically characterized by intrinsic brittleness and defect sensitivity. The origin is the strong covalent bonding which makes activation of slip systems extremely difficult. To enhance the reliability and ductility, two aspects about control of chemical composition and crystal structure of layered ternary transition-metal carbides and nitrides are focused: (1) incorporating third elements like Al and Si into binary transition metal carbides and nitrides; (2) Secondly, designing chemical composition and crystal structure of solid solutions and new materials. The focused layered ternary carbides and nitrides are ceramics with chemical formula of Tn+1ACn (T=Ti, V, Cr, Nb, Zr and Hf; A is a group-A element; n=1, 2, and 3); (TC)nAl3C2 or (TC)nAl4C3 (T=Zr and Hf; n=1, 2, and 3); and T3AlN (T=Zr and Hf). Theoretical and experimental investigations highlighted astonishing merits of studied layered ternary ceramics: on the one hand, they intrinsically possess excellent mechanical, physical and chemical properties of typical carbides and nitrides from ambient to elevated temperatures, especially Nb-Al-C, Zr-Al-C and Hf-Al-C carbides with promising applications up to ultra-high temperature range; and on the other hand, these carbides and nitrides demonstrate much improved damage tolerance, quasi-ductility and machinability compared with their binary counterparts.

CE-4:L07 Microstructure Evolution During the High Temperature Oxidation of Ti2AlN Ceramics

B. Cui*, W.E. Lee, R. Sa, D.D. Jayaseelan, Department of Materials, Imperial College London, London, UK; F. Inam, M.J. Reece, Centre for Materials Research and School of Engineering and Materials Science, Queen Mary, University of London, London, UK

Ti2AlN, like all MAX phases, shows a unique combination of properties between those of metals and ceramics. However, the oxidation mechanism of Ti2AlN ceramics, which is crucial for high temperature use, is not fully understood. In this paper, the phase and microstructure evolution of oxide scale on Ti2AlN ceramics during oxidation in air has been systemically investigated by X-ray diffraction (XRD), field emission gun scanning electron microscopy (FEGSEM), and energy-dispersive spectroscopy (EDS). At temperatures below 1200 °C, layered microstructures formed on Ti2AlN surfaces containing anatase, rutile, and α-Al2O3. At temperatures higher than 1200 °C, more complex layered microstructures formed on Ti2AlN surfaces containing Al2TiO5, rutile, and α-Al2O3. Based on these microstructural observations, an oxidation mechanism for Ti2AlN ceramics is proposed.

CE-4:L08 First-principles Investigation of Formation and Migration of Defects in Layered Ternary Carbides (MAX Phases)

Jiemin Wang*, Jingyang Wang, Yanchun Zhou, High-performance Ceramics Division, Shenyang National Laboratory for Materials Research, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

MAX phases have attracted great interests due to their astonishing properties combining merits of ceramics and metals, such as high modulus, good oxidation resistance, electrical and thermal conductivity and damage tolerance. MAX phases show promising applications in high-temperature, oxidation and corrosion environments, or as cladding material in GIV nuclear reactor. Defect behavior directly affects the phase stability, mass transfer in oxidation process and irradiation damage, which are the key factors responsible for the reliability and oxidation resistance of MAX phases in harsh environments. In this presentation, we determined possible intrinsic defects in MAX phases (in Ti-Si-C and Ti-Al-C systems), and illustrated the stability of intrinsic and impurity point defects with respect to various chemical potentials, as well as migration mechanisms of several point defects. These results are helpful to understand defect behavior, and can stimulate technological applications of MAX phases.

CE-4:L09 Porous Ti3AlC2 as Catalyst Support for Cleaning Vehicle Exhaust

X.H. Wang*, Y.C. Zhou, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

Ti3AlC2 has been identified as a thermal shock resistant, oxidation resistant, electrically conductive ceramic. In particular, it has a close thermal expansion coefficient to the ceramic catalysts for cleaning vehicle exhaust. This can reasonably improve the adhesion of the catalysts to catalyst support, preventing the catalysts from peeling off during critical thermal cycles. As a result, the life time of the catalyst system will be much prolonged. In addition, catalyst support made of Ti3AlC2 can be directly heated because of its electrical properties. Therefore, Ti3AlC2 holds promise for applications as directly-heated catalyst support. Here we report the fabrication of Ti3AlC2 with controlled porosity. Mechanical, electrical, thermal and other properties of the prepared porous Ti3AlC2 are investigated. The dependence of those properties on the porosity and temperature is also presented for the first time.

Session CE-5
Composites for Extreme Environments

CE-5:IL01 Near-net-shape Thermoplastic Forming of Alumina-silicon Carbide Nanocomposites

F. Kern*, R. Gadow, IFKB - Universität Stuttgart, Stuttgart, Germany

Alumina-SiC nanocomposites have attracted the interest of material scientists due to their excellent mechanical and thermomechanical properties. Compared to alumina they offer higher strength, toughness and reliability. The high creep resistence of alumina-SiC makes it attractive for high temperature structural applications. Commercial applications however require performing and reliable manufacturing technologies. Ceramic injection molding (CIM) was chosen for the production of small and complex shaped components with narrow dimensional tolerances used in engineering applications. For axially symmetric, elongated component geometries such as tubes or rods, thermoplastic extrusion is a more appropriate forming technology. This paper is a study carried out to evaluate the complete process cycle of these two thermoplastic forming technologies starting with the aim to evaluate their suitability for industrial production of alumina-SiC nanocomposites. Compounding of the feedstocks, forming by CIM and extrusion and the subsequent thermal treatment - debinding and pressureless sintering were investigated. Intermediate and final products were characterized with respect to rheological properties, structure and mechanical properties.

CE-5:IL02 Ceramic Composites for High Temperature Propulsion System

D.B. Marshall, Teledyne Scientific, Thousand Oaks, CA, USA

The optimization of fiber architecture in ceramic composites has provided new opportunities for the design of aerospace structures and propulsion systems that require lightweight, strong, high temperature materials. The development of textile based composites for application in turbine engine combustors, rocket engines and combined cycle engines will be discussed. Material limitations and degradation mechanisms will also be discussed along with some challenges in simulating aggressive combustion environments in laboratory scale experiments.

CE-5:L03 Evaluation of Fatigue Life of Ceramic Matrix Composites Utilizing Novel Evaluation Technique

K. Toyoshima*, T. Hinoki, A. Kohyama, Kyoto University, Uji, Japan

Fatigue is responsible for the majority of failure in actual components. Fatigue life is generally evaluated by the applied stress and fatigue cycle when materials have completely fractured. Following this conventional evaluation method, even if a great deal of damage is accumulated, fatigue life is satisfied in the stage that composites have not been completely fractured. In the case of the application to airplanes, damage tolerant design is majored, while in the case of nuclear application crack propagation is the fatal factor. Therefore an improved evaluation method is need to be established. In this work, fatigue test was conducted utilizing an advanced evaluation method which focuses on the degradation of apparent elastic modulus which is sensitive to cracks propagation. The object in this work is to find out actual lifetime, in which designed composite properties are substantially maintained. High resistance to fatigue damage is attributed from high resistance to crack propagation depending on low matrix porosity. Fatigue damage accumulation is strongly affected by the difference of reinforcement fiber direction or fabrication technique.

CE-5:L05 Thermal Residual Stresses Generated during Processing of Cr-Al2O3 Composites and their Influence on Macroscopic Elastic Properties

W. Weglewski[1]*, M. Chmielewski[2], D. Kalinski[2], K. Pietrzak[1, 2], M. Basista[1], [1]Institute of Fundamental Technological Research, Polish Academy of Sciences, Warsaw, Poland; [2]Institute of Electronic Materials Technology, Poland

A very important feature of composite materials is that their properties can be tailored according to the targeted application by varying the volume fractions and properties of the matrix and the reinforcement, the type, shape, size, orientation and distribution of the reinforcement, and by controlling the reinforcement/matrix adhesion level. Irrespective of the composite type one of the main problems encountered in their fabrication are thermal residual stresses due to mismatch between thermal and mechanical properties of the matrix and the reinforcement. These stresses may cause microcracking during cooling process of the composite which in turn may negatively affect its properties. On example of Cr-Al2O3 composite processed by powder metallurgy, thermal stresses after fabrication are determined by FEM model for different contents of metal and ceramic phases. Numerical model of microcracking induced by thermal stresses is then proposed and applied to compute the overall elastic properties of the damaged composite. Comparison of the model predictions with the measured data for Young's modulus is presented.

CE-5:IL06 Mechanical Behaviour at High Temperature of Ceramic Matrix Composites and Damage

P. Reynaud*, M. R'Mili, N. Godin, G. Fantozzi, Université de Lyon, INSA-Lyon, MATEIS CNRS UMR 5510, Villeurbanne, France

Self-healing ceramic-matrix composites are interesting materials for long-term uses at high temperatures under air. Lifetimes have been studied under tensile static and cyclic fatigue at intermediate temperatures for composites with SiC fibres or with C fibres. Composites with SiC fibres are sensitive to slow crack growth in the fibres, and composites with C fibres are mainly controlled by recession of interfaces and of fibres. Nevertheless, in both cases the self-healing matrices slow the penetration of oxygen inside the composites and increase the lifetime. To detect damage during these tests and identify the damage mechanisms involved, acoustic emission has been recorded. A non supervised classifier has been developed to separate the classes of signals according to their shape, and assign them to damage mechanisms like fibre break, matrix multi-cracking or fibre/matrix debonding. The global activity of acoustic emission during fatigue tests has been also studied. During the tests, the global activity increases at the beginning then vanished. After a minimum of activity at 60% to 80% of the lifetime, the global activity increases again until the fracture. This minimum of activity and the renewal after are interesting data to correlate with lifetimes.

CE-5:IL07 **Boron Nitride and Boron Nitride Composites for Applications under Extreme Conditions**

J. Eichler*, C. Lesniak, ESK Ceramics GmbH & Co. KG, Kempten, Germany

ESK Ceramics, a subsidiary of Ceradyne Inc., develops and manufactures pioneering products in the fields of advanced ceramics, ceramic powders and frictional coatings. One of the main products of ESK is Hexagonal Boron Nitride (h-BN). BN can be used as powders, coatings or in its sintered form either as pure BN or as a composite. Due to its unique combination of properties BN is an excellent material for applications under extreme conditions. BN is an excellent electrical insulator. It is high temperature resistant, thermal shock resistant, has a high thermal conductivity and a poor wettability for many glass and metal melts. It is chemically inert and non-toxic. The properties of hot pressed BN materials are governed by the BN platelet morphology and the chemistry of the liquid phase. Various BN materials with variations in liquid phase (MYCROSINT® S & MYCROSINT® CD) or purity (MYCROSINT® HD & high purity MYCROSINT®) meet specific challenges under extreme conditions. As a composite with zirconia BN materials are used in the steel production as a side dam material for thin-strip casting (MYCROSINT® O and MYCROSINT® SO). For the metallizing industry BN / titanium diboride composites are used as evaporation boats for aluminium (DiMet® and TriMet®).

CE-5:L08 **Microstructural and Thermo-mechanical Characterization of Yttria Ceramic Cores for Investment Casting, With and Without Particulate Reinforcement**

A. Brentari, M. Villa, E. Leoni, C. Mingazzini*, M. Labanti, S. Sangiorgi, ENEA, Engineering of Components and Processes Section, Faenza Research Centre, Italy

One of the objectives of the MITGEA Italian national project is to develop innovative processes for the industrial production of ceramic cores suitable for the production of the most innovative DS Ni-based superalloys turbine blades. The research activity was aimed at the improvement of the thermo-mechanical properties of ceramic cores. During DS casting process, the ceramic cores are kept in contact with the fused metal, for around 6 hours, at about 1500 °C. These conditions are not easily tolerated by conventional silica ceramic cores, because of insufficient creep resistance. At the moment the technical solution is to produce highly porous silica ceramic cores with high crystobalite content, using coarse grains (up to 150µm) and zirconium silicate particulate as reinforcements. As an alternative, yttria ceramic cores were studied. Yttria is characterized by improved mechanical properties and higher chemical resistance at high temperatures. A commercial powder, with d90 around 10µm, was used to prepare a slurry, before granulation of the powders for pressing. Microstructure, MOR and creep resistance were compared to the corresponding characteristics of commercial silica cores. Submicronic SiC and other reinforcements were tested in order to increase MOR and creep resistance.

CE-5:L09 **Corrosion Resistance Under Wet Atmosphere of Coated and Uncoated Sic-based Composites**

G. Di Vita[1]*, S. Foucaud[1], A. Maître[1], T. Chartier[1], A. Denoirjean[1], O. Preziosa[1], G. Montavon[2], C. Barthélemy[3], V. Laurent[3], D. Lombard[4], [1]Lab. Science des Procédés Céramiques et de Traitements de Surface, UMR CNRS 6638, Université de Limoges, Limoges Cedex, France; [2]LERMPS - UTBM, site de Sévenans, Belfort Cedex, France; [3]Alcan CRV - URA Electrolyse et Matériaux Réfractaires, Voreppe Cedex, France; [4]Alcan LRF, Saint-Jean-de-Maurienne, France

SiC-based ceramics are of prime interest as sidelining materials for electrolysis cells in the aluminum industry due to its chemical stability when in contact with molten aluminum and/or cryolite-based salt melts. Nevertheless, the main damages that occur for long working time proceed from the corrosion under wet air and from the reaction with salt melts. Accordingly, various SiC-based refractories were elaborated by using Spark Plasma Sintering process with different nitride bounding phases. On the basis of the oxidation kinetics achieved under wet air at 1000°C, the role of the bounding phase on the corrosion mechanism of the composite has been elucidated. This was also completed by studying their behaviour in molten cryolite. In the same time, the understanding of the corrosion behaviour of metal oxide coated SiC/Si3N4 ceramics was carried out. The thick homogeneous oxide ceramic coating was elaborated by plasma spraying processing. The potentialities of ceramic coatings as protective layers have been discussed from the comparison of the oxidation kinetics acquired under the most severe conditions (i.e., high water partial pressures) between the coated and uncoated SiC-based materials.

Poster Presentations

CE:P01 **Processing and Characterization of Zr-, Hf- and Ta-based Ultra High Temperature Ceramics**

R. Licheri, R. Orrù, C. Musa, G. Cao*, Dipartimento di Ingegneria Chimica e Materiali, Centro Studi sulle Reazioni Autopropaganti (CESRA), Unità di Ricerca del Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Unità di Ricerca del Consiglio Nazionale delle Ricerche (CNR) - Dipartimento di Energia e Trasporti, Università degli Studi di Cagliari, Cagliari, Italy, IM-Innovative Materials S.r.l., Sestu, Cagliari

MB2-SiC and MB2-MC-SiC (M=Zr, Hf, Ta) Ultra High Temperature Ceramics (UHTCs) are fabricated in this work by combining Self-propagating High-temperature Synthesis (SHS) and Spark Plasma Sintering (SPS). Zr, Hf or Ta, B4C, Si, and graphite powders are first reacted by SHS to successfully form the desired composites. For the case of the Ta-based system, a 20 min ball milling treatment is also required to mechanochemically activate the SHS reactions. The resulting powders are then consolidated by SPS at 1800 °C and P=20 MPa, thus obtaining products with densities greater than 96% within 30 min of total processing time. Hardness, fracture toughness, and oxidation resistance of the resulting dense UHTCs are similar to, and in some cases superior than, those related to analogous products synthesized by alternative, less rapid, methods. Moreover, the ternary composites display relatively low resistance to oxidation as a consequence of the lower SiC content in the composite, in comparison with the binary systems, as well as to the presence of MC. In fact, although the latter ones are potentially able to increase the resistance to ablation of the composites, they oxidize rapidly to form MO2 and carbon oxides which lead to sample porosity increase thus enhancing product oxidation.

CE:P04 **Production and Characterization Alumina-diamond Composites and Nanocomposites**

E.M.J.A. Pallone*, USP, FZEA, Pirassununga, SP, Brazil; V. Trombini, Instituto de Pesquisas Energéticas e Nucleares, Sao Paulo, SP, Brazil; K.L. Silva, L.O. Bernardi, M. Yokoyama, R. Tomasi, UFSCAR-DEMa Sao Carlos, SP, Brazil

The addition of nanometric and/or micrometric particles of a second phase into ceramics matrix is one of the most recent alternatives in the development of materials with high mechanical properties and wear resistance. Nanostructured materials can be defined as systems that have at least one microstructural characteristic of nanometric dimensions (less 100nm). In this work alumina-diamond nanocomposites were produced using diamond nanometric powders obtained by high energy milling in the SPEX shaker/mill during 6h, with a ball-to-mass ratio of 4:1. The crystallite size was 30nm. The composites were obtained using different particles size (1-2 µm, 4-8 µm e 10-20 µm). After the desaglomeration, the diamond powders were added in the alumina matrix in the ratio of 5wt%. The specimens were isostatically pressed and sintering under high vacuum. The obtained nanocomposites and composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), microhardness, diametral compressing and wear resistance. The results showed promising characteristics for the alumina-diamond nanocomposite.

CE:P05 Effects of the Pin-on-disc Test Parameters on the Wear of Alumina

N.R. Tedesco[1]*, E.M.J.A. Pallone[2], R. Tomasi[1], [1]UFSCAR, Sao Carlos, SP, Brazil; [2]USP, FZEA, Pirassununga, SP, Brazil

Searching for wear resistant materials, attention has been paid to Si3N4, SiC, Al2O3 and ZrO2 ceramics. As compared to metals and polymers, these ceramics are inert and present better mechanical and corrosion proprieties, hardness and high-temperature resistance. Although brittleness and low toughness have posed some obstacles to industrial use of the above mentioned ceramics, recent improvements in alumina processing have lessen this restrictions and suggest improvements in wear resistance which in turn have driven some research on this. Since a direct comparison between the many published works regarding this wear improvement is impossible due to the fact wear resistance is a response of the microstructure, material and testing condition, the work herein presented aims to first do a literature review on the main parameters to be controlled in a pin-on-disc apparatus on the wear of alumina and then made some test and analyze the influence of critical parameters as load, sliding speed, sliding distance and environment in a pin-on-disc wear test in a sub micrometer alumina. At the end of this work the procedure followed was indicated.

CE:P08 Structure Evolution in Al2O3 - ZrO2 (Y2O3) Ceramic Composites during Sintering

Ya. Dyatlova*, À. Osmakov, V. Pesin, V. Rumyantsev, VIRIAL Ltd., Saint-Petersburg, Russia

The paper demonstrates the possibility to control the degree of tetragonal zirconia stabilization, microstructure and physical and mechanical behavior of Al2O3 -ZrO2(Y2O3) ceramic composite. Control is exerted via the process variables during deposition synthesis of nanosized composite powders from hydroxide salts, and their subsequent heat treatment and consolidation. Morphology features of nanosized powder systems and microstructures of the consolidated nanostructured materials were characterized by BET surface are measurements, scanning electron microscopy (both standard and HR), and large-angle X-ray diffraction. Correlations are established between microstructure parameters, physical and mechanical behavior of composite ceramics and a degree of stabilization of tetragonal ZrO2.

CE:P09 Fabrication of Reaction-Bonded SiC Composites by Liquid Silicon Infiltration

B.K. Jang*, Y. Sakka, Nano Ceramics Center, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; S.Y. Kim, I.S. Han, S.K. Woo, Convergence Energy Materials Research Center, Korea Institute of Energy Research, Daejeon, Korea

Silicon carbide (SiC) is known to be attractive candidate material for high temperature application, e.g., components of combustion chamber, gas turbines and heat exchangers, because of its good tribological properties, high strength at high temperature, low thermal expansion coefficient and excellent thermal shock resistance. This work describes the microstructure, strength and fabrication of Si-SiC composites by reaction-bonded sintering due to liquid silicon infiltration using C-SiC green bodies and embedded Si. α-SiC powders used in this work are singe or mixed composition of 44 ~1 μm of wide particle size. Carbon black as source of carbon was used. SiC powders, carbon black and organic binder were mixed at different volume ratios and ball-milled in ethanol for 24 h to obtain homogeneous slurries. The typical composition of the green compacts consisted of 60~80 wt% SiC, 20~40 wt% carbon black. Sintered bodies were obtained by reaction-bonded sintering of embedded Si on green compacts at 1500~1600 °C in a graphite furnace of vacuum. Microstructure and morphology of SiC composites were observed by SEM. The reaction-bonded sintered bodies have a high density with <1% of porosity. The effect of microstructure on mechanical properties of composites will be described.

CE:P10 Structural Ceramics Based on Nanosized Si3N4 Powders

V. Rumyantsev, N. Korableva*, À. Osmakov, N. Belykh, VIRIAL Ltd., Saint-Petersburg, Russia; L. Stafeckis, Neomat Co., Salaspils, Latvia

Ceramics based on nanosized plasma chemistry Si3N4 powder compositions s (30-100 nm) is processed by activated pressureless sintering, hot pressing and hot isostatic pressing. Microstructure characterization of the obtained materials by means o light and scanning microscopy revealed no correlation between microstructure and the bulk consolidation method . Average grain size in all cases was 200-500 nm. Comparative characterization of the physical and mechanical behavior of the analyzed samples showed the following results: relative density - over 99%, flexural strength - over 700 MPa, Vickers hardness - 16-17GPa, fracture toughness - 6.5-7.4 MPa·m1/2. The activated pressureless sintered samples demonstrated physical and mechanical behavior comparable to the samples consolidated by other methods. Activated pressureless sintering of na nosized plasma chemistry Si3N4 powders led to considerable economic advantages in processing Si3N4 spherical rotation bodies for hybrid roller bearings and cutting tools.

CE:P11 Stereological Description of Microstructure of Silicon Carbide-based Structural Ceramics as a Composite Material

V. Rumyantsev, S. Boykov, À. Osmakov*, VIRIAL Ltd., Saint-Petersburg, Russia; V. Fischev, Saint-Petersburg State Technology Institute, Technical University, Saint-Petersburg, Russia

Within unified stereological approach the silicon carbide-based ceramics SiSiC , SSiC, and LPSiC are treated as binary compositions, that despite certain structure ordering differences might be similarly described as comprising topologically continuous component (that provides the high level of physical and mechanical properties), and a discrete component. The paper demonstrates the necessity of using dimensionless criterial parameters for adequate description of the integral microstructure ordering level; said parameters including the characteristics of both continuous and discrete components of the composite ceramic material. Generalized equations are derived for compound stereological parameters of the discussed materials, along with statistically reliable approximations of the strength characteristics as functions of these parameters.

CE:P12 Consolidation of SiC Deposits by Polymer Infiltration and Pyrolysis Method

A. Ivekovic*, K. König, S. Novak, G. Drazic, Jozef Stefan Institute, Ljubljana, Slovenia

The polymer infiltration and pyrolisis (PIP) method is used to consolidate SiC deposits prepared by electrophoretic deposition. Due to the high initial density of the deposits (62%) only few cycles were needed in order to achieve a high density material. Microstructures and thermal properties of the material are assessed and compared to the deposits consolidated by standard sintering techniques. Thermal conductivity of the deposits consolidated with PIP was significantly improved in comparison to the deposits consolidated with standard sintering at high temperatures (2373 K) or deposits sintered at low temperatures (1673 K) with the use of transient eutectoid. The influence of microstructure and porosity on thermal conductivity of the material was also evaluated. Although porosity influences the thermal properties of the material to some extend, it is not the governing parameter. Crystallite size and the amount of impurities have shown to have much grater influence on thermal properties of the material.

CE:P13 Processing and Thermal Properties of Cu-AlN Composites

Marcin Chmielewski*, Katarzyna Pietrzak, Dariusz Kaliñski, Institute of Electronic Materials Technology, Warsaw, Poland

Heat transfer by conduction is involved in the use of heat sinks to dissipate heat from the electronic devices. Effective transfer of heat requires using materials of high thermal conductivity. In addition, it requires appropriate values of thermal expansion, matched to the semiconductor materials, high purity of used materials and good contact between bonded elements across which heat transfer occurs. The conventional materials are not able to fulfil the still raising and complex requirements. The solutions of this problem could be composites materials, where the combinations of different properties is possible. This study presents the technological tests and the analysis of correlation between processing parameters and the properties of copper-aluminium nitride composites. The composite materials were obtained by mixing in planetary ball mill and then sintered by hot pressing. The microstructure of obtained composite materials were analyzed by scanning electron microscopy. Coefficient of thermal expansion (CTE) and thermal conductivity (TC) were investigated related to the process conditions.

CE:P14 Diffusion Studies Involving Nanometric and Submicrometric Alumina Based Composites with Gray Cast Iron

K.P.S. Tonello*, V. Trombini, A.H.A. Bressiani, J.C. Bressiani, IPEN, Sao Paulo, SP, Brazil

Machining processes require tool materials with properties such as high hardness at high temperature, high fracture toughness and chemical stability with the workpiece. Advances in science and industry, as well as the development of harder materials have permitted cutting tool technology to evolve. In cutting processes, the contribution of different wear mechanisms to total wear is related to the mechanical and chemical properties of the two materials in contact. The high temperatures at tool-workpiece contact zones often result in diffusion of material from the workpiece to the cutting tool. Diffusion experiments were carried out to understand wear mechanisms involved at cutting edges of ceramic tools and the influence of microstructure on diffusion without the interference of mechanical wear processes. The chemical stability was determined from static interaction couple experiments at 1100°C with ceramic composite materials and gray cast iron. To investigate the influence of grain size on diffusion, sub-micrometric and nanometric alumina based composites with NbC as the second phase were used. These experiments helped demonstrate the influence of grain size on diffusion and the relative inertness of the composites in the presence of gray cast iron.

CE:P15 **Phase, Structural and Microstructural Changes in TiC1-x - Cr3C2 Materials**

P. Rutkowski*, L. Stobierski, M.M. Bucko, AGH University of Science and Technology, Fac. of Material Science and Ceramics, Krakow, Poland

Earlier studies showed that addition of different chromium carbides to nonstoichiometric fine titanium carbide improves sintering in the similar way. The phase, structural and microstructural changes for addition of various chromium carbides were also similar. In the present work composite materials were made of various carbon quantity saturated titanium carbide (as matrix) and commercial chromium carbide Cr3C2 (as additive). The titanium carbide powders with variable content of carbon in the structure were synthesized by SHS. 7.5 vol% chromium carbide was added to the initial mixture. The influence of various stoichiometry of titanium carbide on onset temperature of sintering was examined by high temperature dilatometry. The phase and structural changes of materials during sintering were investigated by XRD and the Rietveld method. The evolution of microstructure, vs different stoichiometry titanium carbides was observed by scanning electron microscopy.

CE:P16 **Influence of Residual Thermal Stresses on the Properties of the NiAl Matrix Composites Reinforced with Ceramic Particles**

Dariusz Kalinski*, Marcin Chmielewski, Katarzyna Pietrzak, Institute of Electronic Materials Technology, Warsaw, Poland

One of the most important problems in both the fabrication and exploitation of ceramic-metal composites are residual thermal stresses. The paper presents the results of a numerical analysis (by the Finite Elements Method)of the stress state induced in the NiAl matrix composites reinforced with spherical particles of a ceramic phase (Al2O3, ZrO2, TiC), including examinations of the dependence of this stress state on the volumetric fraction of the ceramics (20 to 50vol.%). The stress state prevailing in this composite appeared to be complex. In all the samples, the stresses active in the ceramic regions were compressive whereas those active in the metal matrix were tensile in the circumferential direction and compressive in the radial direction. An increase of the ceramic volumetric fraction resulted in an increase of the tensile stresses in the NiAl matrix and a decrease of the compressive stresses in the ceramic particles. These theoretical results were verified experimentally by examining the properties of the NiAl-Al2O3, NiAl-ZrO2 and NiAl-TiC (20 and 30 vol.% fraction of the ceramics) composites produced by hot-pressing. The microstructure, porosity, elastic modulus and bending strength of these composites were examined, and the results are discussed in the paper.

Symposium CF

CERAMICS FOR CHEMICAL, ELECTROCHEMICAL AND ENVIRONMENTAL APPLICATIONS

Oral Presentations

Session CF-1
Ceramics in Chemical and Biochemical Sensors

CF-1:IL01 **Effective Designs for High Temperature Ceramic Gas Sensors**

Prabir K. Dutta, Department of Chemistry, The Ohio State University, Columbus, OH, USA

Solid-state electrochemical devices composed of stabilized zirconia electrolytes (YSZ), e,g, oxygen sensor is used extensively for sensing in combustion environments. However, sensors for detecting other gases have not been as forthcoming. We will present our work in the area of total NOx sensors based on YSZ and catalysis research. In the presence of oxygen, the heterogeneous catalytic reactions occurring on the surface of metal-oxide electrodes and electrolytes compete with electrochemical reactions. We find that the heterogeneous catalytic activity of WO3, yttria-stabilized zirconia (YSZ), and Pt containing zeolite Y (PtY) have a significant influence on the performance of solid-state potentiometric gas sensors. Pt electrodes covered with PtY and WO3 are used as the reference and working electrodes because of the significant reactivity difference, with WO3 being largely inactive toward catalytic NOx equilibration. Using highly catalytic active PtY to filter incoming gas mixtures can effectively remove interferences from 2000ppm CO, 800ppm propane, 10ppm NH3, as well as minimize effects of 1~13% O2, CO2, and H2O. New ways of deposition of electrodes as well as increasing sensitivity to ppb levels will be presented. In addition, we will also review our latest results on high temperature ceramic CO and CO2 sensors.

CF-1:IL02 **VOCs Detection with Potentiometric Oxygen Sensor with Modified Pt Electrode**

Yoshihiko Sadaoka, Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, Matsuyama, Japan

We proposed the use of the modified electrode of Pt with some second materials for potentiometric oxygen sensor to detect sub-ppm levels VOCs in the temperature range of 400 and 550 °C. For all examined sensors, the contamination with ethanol and toluene induced the shift of the EMF. For ethanol, a larger shift of the EMF was observed by the over-coating of Pt with Au (Sensor-2) and the coating with SmFeO3 (Sensor-5) induced a decrease in the EMF response. The coating with SiC (Sensor-3) or Sm2O3 (Sensor-4) induced a larger shift of the EMF in initial period and then slightly recovered. For toluene, the EMF response was clearly influenced by the over-coating and the EMF in toluene was in the order of Sensor-2 ~Sensor-3 > Sensor-4 > Sensor-1 (Pt|YSZ|Pt) > Sensor-5. The observed EMF shifts with the contamination of ethanol suggested a more decrease in the oxygen activity of Au, SiC and Sm2O3-coated electrode than that of Pt electrode and the coating of Pt electrode with SmFeO3 depressed a decrease in the oxygen activity by the ethanol contaminations. For toluene, the coating on the Pt electrode induced a more decrease in the oxygen activity on the TPB site in the order of Au > SiC > Sm2O3 > SmFeO3.

CF-1:IL03 **Plasmonic Based Harsh Environment Compatible Chemical Sensor**

Michael A. Carpenter, College of Nanoscale Science and Engineering, University at Albany, NY, USA

The development of novel harsh environment compatible chemical sensing technologies is a critical need for a variety of combustion applications. The plasmonic properties of embedded gold nanoparticle (AuNP)s in yttria stabilized zirconia (Au-YSZ) nanocomposite films is a promising sensing material. The AuNP surface plasmon resonance (SPR) band was monitored as concentrations of O2, H2, NO2 in N2, were varied at elevated temperatures (~500 °C). Detectable changes in the SPR band were observed for all of the gases. Extensive titration experiments have been performed and will detail the interfacial charge transfer reactions occurring at the tri-phase boundary. An electrochemical model is developed which correlates changes in the free electron density with the reaction gas mixture and also determines the free energy change upon reaction. Kinetics experiments probing interfacial reactions have been used to further develop an understanding of the interfacial reactions. A 10ppm detection limit for NO2 in air at 500°C has been achieved, however, a study of the reaction dependence on the size of the AuNPs within the matrix enables the sensitivity of these materials to be increased by orders of magnitude. Experiments with other metal oxides will also be detailed.

CF-1:L05 Novel Architectures for Gas Sensing through Semiconductor Thin Films Containing Au Nanoparticles with Highly Controlled Morphology

A. Martucci*, E. Della Gaspera, Università di Padova, Italy; M. Post, NRC-Ottawa, Canada

Gas species recognition through fully optical devices is currently a raising trend over the well established conductometric approach, as it opens new possibilities especially for in situ recognition of flammable and/or toxic species such as H2, CO and H2S. Catalytically active nanoparticles (NPs) inside a porous semiconductive matrix constitute an effective design for a sensor's active material, and Au NPs show promising chemical and optical properties exploitable in sensing devices. We present here some strategies for the synthesis of highly reproducible semiconductors thin layers (TiO2 and NiO) containing elevated concentrations (up to 8% wt) of separately synthesized Au NPs for optical gas sensing purposes. TiO2-Au thin films were obtained by direct insertion of Au NPs into the matrix precursors solution through a careful control of the matrix network-NPs electrostatic interaction. NiO-Au thin films were obtained spin coating a NiO precursors solution on a glass surface previously functionalised with a close-packed Au NPs monolayer. All the samples showed detectable and reversible change in optical absorption when exposed to H2 and CO species. It is the first time that a gas induced optical property variation was detected for the TiO2-Au system in a thin film configuration.

CF-1:L06 Effect of the Electrode Morphology on the Sensing Characteristic of the YSZ Based Potentiometric Oxygen Sensor

M. Mori*, Y. Kojima, Y. Sadaoka, Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, Matsuyama, Japan

Electrochemical devices based on an oxygen ionic conductor (8 mol% Y2O3-stabilized ZrO2: 8YSZ) fitted with Pt and Au electrodes were investigated. For electrodes, platinum paste and gold paste were printed on one side of the YSZ-sheet and heated at 500-800 °C for 1h. The dependence of the electromotive force (EMF) on oxygen concentration and the EMF to ethanol and toluene were measured at 400-550 °C. The sensor heated at 700 °C showed the highest sensitivity to 0-21 % oxygen and VOCs. The EMF change of this sensor in 21 % oxygen and nitrogen at 400 °C was 0.03 V and 0.45 V respectively. It means that the oxygen ion activity at Pt and Au electrodes was not so different in 21% oxygen atmosphere, while the oxygen ion activity at the Au/YSZ interface was much lower than that of the Pt/YSZ interface in nitrogen. It concludes that the developed device can be applied for VOCs sensor. The ΔEMF to 0.5 ppm ethanol and toluene was both 0.23 V at 400 °C.

CF-1:L07 CVD of Tin Oxide Nanowires: Growth, Structure and Property

Sanjay Mathur, Hao Shen*, Institute of Inorganic and Materials Chemistry, University of Cologne, Cologne, Germany

One-dimensional (1D) nanoscale materials, such as nanotubes (NTs), nanowires (NWs), and nanobelts (NBs), have attracted significant attention due to their unique size- and dimension-dependent electrical, optical, chemical and mechanical properties. As a n-type direct wide band semiconductor (Eg = 3.6 eV at 300 K), SnO2 is a key functional material that has been used extensively for gas sensor, optoelectronic devices, catalyst supports, transparent conducting electrodes and antireflective coatings, while responding to the test gas, which effectuates the differential sheath conductivity as a function of the analyte gas concentration. Although a lot of studies have synthesized tin oxide nanowires in random form, few works have focused on the development of ordered nanowires. We present here that tin oxide nanowire arrays on titania (001) can be successfully fabricated by using of CVD of Sn(OtBu)4 precursor. The diameter/length of ordered nanowires was well controlled by variation of precursor/substrate temperatures and size of gold catalyst. The morphologies and structures of SnO2 were analyzed by SEM/EDX, HR-TEM and XRD. The cross-sectional TEM analysis showed the epitaxial growth of tin oxide nanowires from titania substrate. The wires prefer to [101], [-101], [011] and [0-11] growth directions due to the lowest surface energy. A growth model for the nanowire arrays based upon crystallographic relation and preferential growth direction is proposed. The abnormal oblique interface (ca. 67.8o) between SnO2 and the Au droplet indicates the atomic layer-by-layer growth of SnO2 NWs along the [101] direction. The studies on the electrical and gas sensing properties of SnO2 [101] single nanowire showed that the nanowire arrays can be potentially used as diameter- and orientation-dependent sensing unit for detection of gas molecules. Response vs. concentration log-log plot showed the linear sensing characteristic behavior of SnO2 [101] nanowire.

Session CF-2

Ceramic Membranes and Filters

CF-2:IL01 Ceramic Hollow Fiber Gas Separation Membranes for Sustainable Energy Production

F.M.M. Snijkers*, C. Buysse, A. Kavaleuski, J.J. Luyten, A. Buekenhoudt, Flemish Institute for Technological Research (VITO), Mol, Belgium

Sustainable energy production from fossil fuels requires the use of novel technologies for capture and storage of CO2. Gas separation membranes, which are associated with significant lower efficiency losses compared to conventional gas separation technologies, can play an important role in achieving this. Promising membrane materials are oxygen-permeable perovskites with mixed ionic-electronic conduction. When exposed to an oxygen chemical potential gradient at high temperatures (>700 °C), they show a 100% selectivity for oxygen, without the need for electrodes and external electrical circuit. Furthermore, their inherent high temperature operation is advantageous for integration in high temperature combustion processes. Since large-scale gas separation applications demand high surface/volume ratios, membranes with capillary or hollow fibre geometry have a distinct advantage over tubular and flat sheet membranes. In this work we present results of the fabrication and performance of Ba0.5Sr0.5Co0.8Fe0.2O3-d (BSCF) capillary membranes, fabricated by a spinning technique based on phase inversion. The fabrication of gastight capillaries will be described. In addition to results of oxygen permeation measurements of BSCF hollow fiber membranes, preliminary results on the modeling of oxygen permeation through BSCF capillaries and hollow fibres will be shown.

CF-2:IL02 The Environment Improved by the Use of Ceramic Membranes and Filters

J. Luyten*, S. Mullens, F. Snijkers, A. Buekenhoudt Materials Technology, VITO, Boeretang 200 , B-2400 Mol, Belgium

In the 21st century, life on earth will be strongly affected by energy and environmental issues. Water and air will have to be cleaned and materials have to be recycled and re-used. To realize these needs specific tools have to be developed. In this contribution, the focus is on porous ceramic structures, ceramic membranes and ceramic foams as contributing means to handle the environmental issues of the future. At first we discuss the synthesis and characterization of multilayer ceramic membranes for solvent and gas separation. The processing of different membrane types, e.g. nanofiltration membranes, zeolite membranes and dense mixed ion electron conducting ceramic membranes is explained. These kind of membranes can be used to recover catalysts and solvents and to make energy production processes more efficient. Secondly ceramic foams that are considered for a widespread variety of applications are discussed. Different manufacturing routes are described with their advantages and disadvantages. More specially we discuss the application of diesel particulate filters (DPF), honeycombs and foams for transport vehicles. The recycling of Al-alloys using a ceramic foam filter will be presented as a special case whereby a liquid metal is purified. The optimization of these materials manufacturing routes requires a good synergy with the characterization of the obtained products at different stage of their processing. As such, a variety of specific characterization techniques is presented in line with the development of the functionalized porous ceramic products.

CF-2:IL03 **Dense Ceramic Membranes for Oxygen Separation**
Henny J.M. Bouwmeester, Inorganic Membranes, Membrane Technology group, University of Twente, Enschede, The Netherlands

Among novel technologies under development as cost-effective alternatives to conventional oxygen production methods, ceramic membranes fabricated from mixed ionic-electronic conducting oxides offer great promise. These membranes selectively separate oxygen from an air supply at elevated temperature (700-1000 °C) under the influence of an oxygen chemical potential gradient. Besides their use in schemes for oxygen production, the membranes have attracted much interest for the conversion of natural gas into syngas (CO + H2) and for integrating in oxyfuel and pre-combustion power generation technologies for CO2 capture. Crucial to the performance is that the ceramic membranes are capable of fast surface oxygen exchange and bulk ionic diffusion, and maintain their structural and chemical integrity under the conditions of application. The present paper highlights new developments and challenges faced in this research field. The paper also discusses oxygen transport properties, oxygen nonstoichiometry, and phase stability of membranes derived from Ba05Sr0.5Co0.8Fe0.2O3 (BSCF) and related perovskite oxides. Particular attention is drawn to chemical expansion and creep behavior of these solids, and the influence of CO2 adsorption on the kinetics of surface oxygen exchange.

CF-2:L04 **Ceramic Foams with Hierarchical Porosity from Preceramic Polymers**
Cekdar Vakifahmetoglu, Paolo Colombo*, Dipartimento di Ingegneria Meccanica - Settore Materiali, Università di Padova, Padova, Italy; J. Woltersdorf, E. Pippel, Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

Open cell SiOC foams with a porosity ranging from about 60 to 85 vol% were fabricated by in-situ catalyst-assisted-pyrolysis using polysiloxane preceramic polymers, azodicarbonamide, as a physical blowing agent, and iron or cobalt catalysts. Depending on the nitrogen or argon pyrolysis atmosphere, nano-wires of silicon nitride or silicon carbide, respectively, were obtained with both catalysts on the inner surface of the pores, directly upon heating, via reaction/condensation processes occurring in the gases developed during processing. Various characterizations were performed on the resulting components, including the measurements of the specific surface area, compression strength, porosity amount and average cell size. Nanocomposition and microstructure were elucidated by XRD and HRTEM investigations combined with EELS and EDXS methods, enabling also to ascertain the particular growth mechanisms.

CF-2:L05 **Development of Acicular Mullite Filters Designed for Filtration of Diesel Particles and Reduction of NOx**
Aleksander J. Pyzik*, Rob Ziebarth, Chan Han, The Dow Chemical Company Midland, MI, USA

Broad implementation of diesel engines requires significant reduction of NOx and particulate matter (PM) from engine exhaust. These requirements, mandated by EU and NA environmental regulations, are satisfied today by an aftertreatment system where NOx reduction and soot oxidation catalysts are deposited on separate ceramic substrates. Today's trend to combine these functions into one substrate has potential for reducing system size and overall cost. However, the large amount of catalyst needed for NOx control (Lean NOx Trap or Urea SCR) reduces porosity and increases back pressure, thus increasing fuel consumption. This paper describes development of the experimental ultra-high porosity acicular mullite ceramic to be used for combined NOx reduction and filtration of soot in diesel engines. Acicular mullite honeycombs having porosities between 65 and 80% showed high strength, excellent NOx reduction and pressure drop that is comparable to state of art commercial filters without any catalyst coating. The effect of increased porosity on mechanical properties, especially on flexural strength, are investigated and discussed in comparison to other high porosity ceramics. The ability to combine several functions into one substrate provides the promise of lower cost for the entire emission treatment and creates an opportunity for other applications requiring highly porous but mechanically strong scaffold as a carrier for functional materials.

CF-2:IL06 **Hydrogen-permselective Amorphous Silica-based Membranes**
Yuji Iwamoto, Department of Frontier Materials, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Japan

This paper describes recent progress in the development of hydrogen permselective amorphous silica-based membranes derived from organometallic precursors. Microstructure and gas transport property of microporous amorphous silica-based membranes are briefly described. Then, high-temperature hydrogen permselectivity and hydrothermal stability of the amorphous silica-based membranes are discussed from a viewpoint of application to membrane reactors for conversion enhancement in the methane steam reforming reaction, which leading to development of a highly efficient hydrogen production system. Novel transition metal-doped amorphous silica-based membranes with a unique hydrogen permselectivity, and polymer-derived amorphous Si-(B)-C-N membranes having enhanced thermal and chemical stability are also discussed from a view point to develop novel ceramic membranes for high-temperature separation of hydrogen.

CF-2:IL07 **Elaboration and Modification of Ceramic Membranes for Filtration Processes**
Sophie A. Cerneaux, André B. Larbot, David Cornu*, IEM, UMR 5635, site CNRS, Montpellier cedex, France

Porous ceramic membranes are used in numerous industrial applications due to their thermal and chemical resistances and stability over a wide pH range. The classical elaboration techniques are extrusion of a ceramic paste for the macroporous support that provides the mechanical resistance, followed by dip-coating or slip-casting of colloidal or polymeric sols (sol-gel process) for the MF, UF and NF layers. Modification of ceramic membranes is of prime interest to overcome environmental and economical problems in wastewater treatment, desalination, solvent purification and emulsion breaking. We focused our interest on the development of capillary and hollow fibres ceramic membranes to increase the surface area to volume ratio and then the packing density to reach high selectivity and high flux per unit volume of module. We designed ceramic capillary supports in cordierite, with outer and inner diameters of 3.3 and 1.5 mm, respectively, a porous volume of 45 % and pore diameters around 6.2 µm. We also modified these ceramic membranes by covalent grafting of perfluorinated alkoxysilanes to prepare a range of hydrophobic membranes. Results concerning elaboration and modification of these membranes will be presented for desalination application essentially.

CF-2:L08 **Influence of Oxygen Surface Exchanges on Oxygen Semi-permeation Performances of La1-xSrxFe1-yGayO3-d Membranes**
A. Vivet*, P.M Geffroy, V. Coudert, T. Chartier, CNRS-ENSCI-SPCTS, UMR 6638, Limoges, France; P. Del Gallo, N. Richet, Air Liquide, Centre de Recherche Claude-Delorme, Jouy-en-Josas cedex, France

Mixed conducting ceramic membranes present a great interest for the methane reforming into synthesis gas at high temperature (900 °C), which constitutes a major solution for the production of hydrogen or clean fuels. The reactor is constituted of a dense ceramic membrane on which a porous layer can be deposited. The La1-xSrxFe1-yGayO3-d perovskite formulations exhibit a good compromise between oxygen semi-permeation and chemical/mechanical stability under such working conditions. The performances of the membranes are evaluated using oxygen permeation flux measurements in relation with the temperature under a gradient of oxygen partial pressure. An original device has been set up to dissociate oxygen bulk diffusion and surface exchange kinetics. This apparatus is constituted of two electrodes, one made of zirconia and the other one made of platinum to measure oxygen potential difference between the surface of the membrane and the surrounding atmosphere. Thanks to the results obtained, new ways for improving oxygen diffusion through the membrane were followed with the coating of a porous layer by screen-printing on the membrane surface. The influences of the porosity and addition of catalytic agent in the porous coating on oxygen semi-permeation performances are studied.

Session CF-3
Catalysts and Catalysts Supports

CF-3.1 Ceramic Catalysts

CF-3.1:IL01 **Aerogel Catalysts**
A.C. Pierre, Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Villeurbanne, France

Aerogels are largely mesoporous solids, with a porosity which often exceeds 90 vol%, a specific surface area up to 1000 m2 g-1. Such materials were first obtained by Kistler in 1932, to designate gels in which the liquid was replaced with a gas without collapsing the gel solid network. Contrary to xerogels dried from wet gels by evaporation with an important shrinkage, the first aerogels were obtained by a "supercritical drying" technique in which the liquid which impregnated the gels was evacuated after being transformed to a supercritical fluid. The variety in the nature of the solids constituting the rigid network is very large. It includes simple oxides, multi oxide compositions, organic and hybrid organic-inorganic polymers and carbon. This variety as well as the high specific pore volume and surface area make aerogels applicable either as catalysts or as catalyst supports. Besides, molecular catalysts such as transition metal complexes or enzymes can easily be immobilized in aerogels. This opens the road to new supported molecular catalysts and biocatalysts, applicable in chemical or biochemical reactions and in sensors. This presentation reviews aerogel catalysts, their synthesis and properties, with special focus on the immobilized molecular catalysts.

CF-3.1:IL02 Highly Efficient Visible Light Photocatalysts on the basis of Interfacial Charge Transfer and Multi-electron Oxygen Reduction Catalyst

Kazuhito Hashimoto, University of Tokyo, Tokyo, Japan; Hiroshi Irie*, University of Yamanashi, Yamanashi, Japan

We recently reported a novel visible-light-sensitive photocatalyst by grafting Ti(IV)-O-Ce(III) hetero-bimetallic assemblies onto the inner walls of mesoporous silica and demonstrated that photocatalytic oxidative decomposition can be initiated by a metal-to-metal charge transfer[1]. Based on this result, we hypothesized that photoirradiation also induces charge transfer directly from an oxide VB to atomic metal ions atomically grafted on the oxide surface. In addition, we paied attention that Cu(I) ion occasionally catalyzes multi-electron oxygen reduction. By combining those considerations, we designed novel photocatalysts sensitive to visible light, namely, Cu(II)-grafted TiO_2 and WO_3 [2, 3]. The fabricated photocatalysts decomposed gaseous 2-propanol to CO_2 very efficiently under visible light. In addition, we found that these photocatalysts show strong anti-virus effect under room light condition.

[1]R. Nakamura, A. Okamoto, H. Irie, K. Hashimoto, J. Am. Chem. Soc. 129 (2007) 9596; [2]H. Irie, S. Miura, K. Kamiya, K. Hashimoto, Chem. Phys. Lett., 457 (2008) 202; [3]H. Irie, K. Kamiya, S. Miura, K. Hashimoto, J. Phys. Chem. C. 113 (2009), 10761.

CF-3.1:IL03 Catalysts Supports for Energy Conversion Processes

J.L.G. Fierro, Inst. de Catalisis y Petroleoquimica, CSIC, Madrid, Spain

Ceramic materials either along or with additional functionality, i.e. catalytic, as well as filter materials and membranes are in use but offer considerable potential for more impact. This contribution aims to provide a general overview of the potential of ceramic materials in several areas related to energy production and storage. Reliable high-temperature membranes with the desired separation efficiency for hydrogen from gas mixtures have been developed over the last decades. After suitable modifications, they show promise for hydrogen separation from gasification streams. In addition to assuring high permeance and selectivity to H2 from syngas, the research is being directed toward determining how to initiate the water shift reaction. Engineered, porous, ceramic support loaded with noble metals are particularly suited to address the material limitations encountered with wash-coated, metal-based, catalyst supports. These materials demonstrated high-performance, coke-resistant, steam methane reforming (SMR) activity. Metal oxides and metal carbides present high stability in a fuel cell environment and acceptable electrical conductivity, but most of them possess a low specific area. In addition, H2 production by water splitting on ceramic oxides of the type ferrites, YSZ and Fe-YSZ will be examined. Finally, a few aspects of the new nanoscale ceramics for batteries of higher storage capacity, storage capacitors and for hydrogen storage will also be presented in this contribution.

CF-3.1:L04 Effects of Surface CeO_2 Particle Size on Diesel Particulate Oxidation of Pr_6O_{11} Based Oxide

Tatsumi Ishihara*, Seiji Hamamoto, Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan

Diesel engines have high fuel efficiencies and are attracting much interest concerning decreasing CO_2 emissions. However, they have a serious drawback of relatively high emissions of particulate matter (PM) and nitrogen oxides (NOx). A PM filter is a kind of porous ceramic material consisting mainly of SiC and a metallic component. For continuous operation, trapped carbonaceous materials in the PM filter must be removed regularly by feeding a fuel spike at which GSHV is corresponded to a value from 10,000 to 100,000 h^{-1}. A number of researchers are now investigating the possible oxidation of soot using a low temperature ignition catalyst in combination with a ceramic PM filter. In this study, effects of dopant and promoter on oxidation activity to carbon upon Pr_6O_{11} based oxide were investigated. It was found that $Pr_{4.8}Bi_{1.2}O_{11}$ is highly active to carbon oxidation and oxidation of graphitic carbon occurs at 550 K at tight contact mode, which is much lower than that of the CeO_2 based conventional catalyst. Furthermore, loading of CeO_2 promoter is highly effective for decreasing the ignition temperature of $Pr_{4.8}Bi_{1.2}O_{11}$ to carbon oxidation. The actual diesel soot can be oxidized at temperature as low as 473 K using $CeO_2/Pr_{4.8}Bi_{1.2}O_{11}$ in the presence of CO_2 and H_2O.

CF-3.1:L05 Ultra-divided Catalysts Tailored for Industrial Steam Reforming Processes

C. Bonhomme*, R. Faure, S. Goudalle, F. Rossignol, T. Chartier, CNRS-ENSCI, Lab. de Sciences des Procédés Céramiques et de Traitements de Surface (SPCTS), UMR CNRS 6638, Limoges, France; C. Bertail, P. Del-Gallo, Air Liquide, CRCD Research Center, Jouy-en-Josas, France

Deactivation of supported catalysts is a major cause of steam reforming unit shut-down in industry. This work is focused on the development of new supported ultra-divided catalysts with improved multiscale structural organization that can fit with the requirements of industrial SMR processes in terms of temperature, pressure and atmosphere for a better effectiveness as well as an additional lifetime. The catalyst support developed here is a spinel-based material (MgAl2O4) prepared by sol-gel synthesis in the presence of a surfactant. The sol is dip-coated on an alumina dense carrier. After calcination at 900°C, a highly divided spinel coating with a controlled porosity is formed. The spinel coated alumina is then impregnated with a rhodium nitrate solution. The porosity presents the advantage to chemically and/or physically entrap active Rh nanoparticles. The stability of this catalyst is characterized before and after 48 hours ageing under SMR-like conditions by XRD, FEG-SEM, TEM, BJH and TPR-TPO. In this work, the demonstration of the possible use of such catalyst inside SMR micro-reactors is established.

CF-3.1:L06 Cobalt-supported Alumina or Clay as Catalytic Film Prepared by Electrophoretic Deposition for Hydrogen Release Applications

R. Chamoun[1, 2]*, U.B. Demirci[1], D. Cornu[3], Y. Zaatar[2], A. Khoury[2], P. Miele[1], [1]Université Lyon 1, CNRS, UMR 5615, Lab. des Multimatériaux et Interfaces, Villeurbanne, France; [2]Université Libanaise, Fac. des Sciences II, Lab. de physique appliquée, Jdeidet El Metn, Liban; [3]Université Montpellier 2, CNRS-ENSCM, UMR 5635, Inst. Européen des Membranes, Montpellier, France

Because shaped catalysts are crucial in many catalytic applications, especially in the view of technological applications, we have developed, for the first time, cobalt supported over alpha alumina catalytic films deposited over copper plates. The films preparation was only considered through electrophoretic deposition. The as-obtained shaped catalysts were intended to be used in hydrogen generation by hydrolysis of sodium borohydride NaBH4 in highly alkaline solution. The Co-Al2O3 films were in fact prepared following to several routes. Whereas most of the studied routes failed in fabricating adhering films, one route showed promising results. Despite a moderately heterogeneous surface, the as-obtained shaped catalysts showed good adhesion as well as good stability in highly alkaline medium. Furthermore, the films were stable and adhering when hydrogen vigorously bubbled at their surface. Finally, cobalt on these films catalyzed the NaBH4 hydrolysis with attractive hydrogen generation rates. Our results show that the successful route we developed is an alternative route for preparing shaped catalysts in this reaction. Our main results will then be presented at CIMTEC 2010.

CF-3.1:L07 BaYMn2O5+d: A Potential Material for Oxygen-Storage Applications

Teruki Motohashi*, Taku Ueda, Y. Masubuchi, Shinichi Kikkawa, Graduate School of Engineering, Hokkaido University, Sapporo, Japan; Makoto Takiguchi, Tohru Setoyama, Mitsubishi Chemical Group, Science and Technology Research Center, Inc., Yokohama, Japan

Oxygen-storage materials (=OSMs) which store and release oxygen reversibly at moderate temperatures have attracted great interests, due to increased demands of regulating oxygen partial pressure in the gas phase. The CeO2-ZrO2 solid solution (so-called "CZ") is the best-known OSM that has been practically used as a three-way catalyst for the effective removal of NOx, CO, and hydrocarbons from automobile exhausts. OSMs may also be applicable to various applications, e.g. oxygen scavengers for inert-gas purifications and oxidizing agents in anaerobic processes. To open up the possibility of such applications, novel OSMs with excellent characteristics are highly desirable. In this contribution, we report remarkable oxygen-storage capability of a double perovskite BaYMn2O5+d. Our thermogravimetric study revealed that this oxide rapidly stores/releases a large amount of oxygen (> 3.7 wt%)

at 500C in a highly reversible manner. The oxygen intake/release behaviors are clearly beyond those of any conventional oxides in terms of the magnitude and sharpness of the processes, which make this material a potential candidate for oxygen storage applications.

CF-3.1:L08 **Metal Oxides as Catalyst Supports for Hydrogen Release by Solvolysis of Boron Hydrides**

O. Akdim, U.B. Demirci*, P. Miele, Université Lyon 1, CNRS, UMR 5615, Laboratoire des Multimatériaux et Interfaces, Villeurbanne, France

Metal oxides are common materials in catalyst preparation. It is generally expected (i) they favor the dispersion of a metal (e.g. Co) while they hinder its aggregation (geometric effect), and (ii) they modify the metal reactivity (electronic effect). Investigating hydrogen release by solvolysis (hydrolysis / methanolysis) of boron hydrides (sodium borohydride / ammonia borane), we have developed metal oxide-based catalysts (Al2O3, TiO2, CoxBy.) to be used as heterogeneous catalysts in these reactions. In most cases, Co was dispersed over the oxide by impregnation. The boron hydrides studied are known to be reducing and the challenge has been to find an oxide stable in such reducing medium. Globally most of the prepared catalysts showed attractive catalytic reactivity in one-shot tests. High hydrogen release rates were achieved, with values being among the highest ever reported. But these performances were only achieved with fresh catalysts. Used catalysts were not as reactive, the reactivity dramatically decreasing with successive shots. Further, the oxides we studied showed different behaviors, the ones being stable in the reducing medium, the others being not. The CIMTEC 2010 congress will then be an opportunity to discuss these behaviors.

CF-3.1:L09 **High Activity Photocatalyst Powder Formed by Three Ceramic Oxides**

L. Perazolli[1]*, G.F. Pegler[1], R.A.J. Ingino[1], M.R.A. Silva[2], M.O. Orlandi[1], M.A. Zaghete[1], J.A. Varela[1], [1]UNESP, Araraquara Chemical Institute, Araraquara, São Paulo, Brazil; [2]Itajubá Federal University, Itajubá, Minas Gerais, Brasil

A Photocatalyst ceramic powder that presented high photoactivity based on TiO_2 modified with 25% molar of SnO_2 and up to 5% molar of Ag_2O was obtained in the present work. The aforementioned ceramic powder was gotten using all commercial oxides as well as the oxides mixture technique. The powders were ground in high energy mill for one hour with subsequent thermal treatment in 400 °C for four hours. They were, furthermore, characterized by surface area around $6m^2/g$, where the DRX results provided evidence for the presence of anatase and rutile phases, known to be typical characteristics of both the TiO_2 and SnO_2 used. During the thermal treatment, Ag_2O was reduced to metallic silver. The photodegradation rehearsals were carried out using a 0.01 mmol/L Rhodamine B solution in a 100mg/L photocatalyst suspension in a 500ml beaker, which was irradiated with 4W germicide Ultraviolet light of 254nm. In addition, samples were removed after about 5 minutes to an hour, where they were analyzed thoroughly in UV-vis spectrophometer. The analysis of the results indicated that for the compositions above 0.5% molar of Ag_2O, the photoactivity was found to be greater than that of P25 Degussa photocatalyst powder, which was then used as a reference. Taking into account 90% degradation of Rhodamine B, a duration period of 12 minutes was obtained for the developed photocatalyst powder compared to the 30 minutes observed for the Degussa P25. FEG-SEM micrographies enabled the verification of the morphology as well as the interaction of the oxide particles with the metallic silver, which led us to propose a model for the increase in photoactivity observed in the photocatalyst powder under investigation.

CF-3.2 Catalysts Supports

CF-3.2:IL01 **Effect of Oxides Composite Support of Ce(Sm)O3-La(Sr)CrO3 on Pd-Ni Alloy for Decomposition Activity of CH4**

Ichiro Yamanaka*, Yuta Nabae, Tokyo Institute of Technology, Department of Applied Chemistry, Tokyo, Japan

Direct conversion of dry CH4 fuel at the anodes in solid oxide fuel cells has received a great deal of attention for efficient conversion of chemical energy to electric power. Major problem is a large amount of carbon deposition on the anodes. Recently, we have found that a Pd-Ni alloy catalyst supported on La(Sr)CrO3 and Ce(Sm)O2 composite anode shows good performance with dry CH4. The purpose of this study is to explain clearly the high tolerance of the Pd-Ni alloy catalyst on La(Sr)CrO3-Ce(Sm)O2 support to the carbon deposition. In catalytic decomposition of dry CH4, carbon deposition was remarkably suppressed on Pd-Ni/Ce(Sm)O2 and Pd-Ni/La(Sr)CrO3 catalysts, whereas Pd-Ni/SiO2 and Pd-Ni/carbon catalysts were very active for the formation of carbon nano-fibers. The Pd-Ni particles on SiO2 and carbon were quite multifaceted from TEM-EDS observation. The surface of the multifaceted particles could be one or some of the (111), (110) and (100) planes of the Pd-Ni alloy. On the other hand, the Pd-Ni particles on Ce(Sm)O2 support had a spherical shape and doping of Ce and Sm was confirmed. This nature should inhibit the formation of particular plane that is essential for the carbon formation. The detail function of Ce(Sm)O2 and La(Sr)CrO3supports will be discussed.

CF-3.2:IL02 **Soot and Ash Layer Characteristics in Ceramic Diesel Particulate Filters**

P. Dimopoulos Eggenschwiler*, A. Liati, Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for I.C. Engines, Duebendorf, Switzerland

Diesel particulate matter (soot) can easily be removed from the exhaust streams by means of filtration using Ceramic Diesel Particulate Filters (DPF). The filtered soot has periodically to be removed from the filter during a process commonly known as “regeneration”. Regeneration of the filtered soot mainly occurs via oxidation processes. Conditions typical for diesel exhaust are not very favorable for oxidation. Although there is no lack of oxygen, the low temperatures prevailing impose a critical impediment. Diagnostic techniques concerning the soot and ash deposition, accumulation and reduction are limited and laborious. X-ray tomography provided information concerning the ash accumulation while electron microscopy was used for quantifying the soot and the ash layer. Apart from the soot deposition, soot nanostructure is strongly affecting soot oxidative behavior. High resolution electron microscopy provided insights of the soot nanostructure such as graphene layer size, tortuosity, separation and orientation. In parallel, Raman spectra reveal size and defects in the basal plane of individual graphene layers, while FTIR spectra have been used to determine the relative amount of oxygen functional groups at the soot surface.

CF-3.2:IL03 **VOCs Oxidation on CeO2-based Catalysts**

T. Masui*, N. Imanaka, Osaka University, Suita, Osaka, Japan

Volatile organic compounds (VOCs) are organic chemical compounds such as aldehydes, ketones, and other light weight hydrocarbons. As they have relatively high vapor pressures under ambient conditions, they vaporize easily and diffuse into the atmosphere. Some VOCs are harmful to human health and the environment, as recognized to cause air pollution such as photochemical smog, ground-level ozone, sick building syndrome, and multiple chemical sensitivity. In this study, Pt/CeO2-ZrO2-Bi2O3 catalysts for catalytic combustion of ethylene, toluene, and acetaldehyde, which are typical volatile organic compounds (VOCs), were prepared by a wet impregnation method in the presence of polyvinylpyrrolidone K25 (PVP). The addition of PVP in the preparation process was effective not only to enhance the specific surface area, but also to increase the Pt2+ ratio on the surface of the catalysts. Additionally, the pore volume and size of the catalysts were modified by the PVP addition. The Pt/CeO2-ZrO2-Bi2O3 catalysts are specific for the total VOCs oxidation and only carbon dioxide and steam were produced by the oxidation. By the optimization of the amount of platinum, the complete oxidation of ethylene, toluene, and acetaldehyde was realized at 65 °C, 120 °C and 140 °C, respectively.

CF-3.2:IL04 **TiO2 Photocatalysis - Fundamental and Recent Situation**

A. Fujishima, Kanagawa Academy of Science and Technology, Kawasaki, Kanagawa Pref., Japan

The tremendous amount of research that has been carried out in the two closely related fields of semiconductor photoelectrochemistry and photocatalysis during the past three decades continues to provide fundamental insights and practical applications. The principles and measurements obtained TiO2 with photoelectrochemical studies have led to the research activity on heterogeneous photocatalysis, where the strong photooxidative activity of TiO2 has been applied to environmental cleanup. This resulted in the concept of “light cleaning,” i.e., deodorizing, disinfection, and decontamination of air, water, and surface with TiO2 thin films and light. In 1997, we reported the novel photo-induced superhydrophilicity of TiO2 and proposed the concept of self-cleaning superhydrophilic properties of TiO2. In this lecture, I will follow the history of TiO2 photocatalysis, outline the contribution of photocatalysis to a comfortable and safe urban environment, and highlight some important points related to the future development of photocatalysis, including the problem of utilizing visible light and the standardization of photocatalytic systems. I will also present some of our recent studies on novel photocatalyst materials and applications.

CF-3.2:L05 **Foam-supported Catalysts Tailored for Industrial Steam Reforming Processes**

R. Faure*, T. Chartier, F. Rossignol, SPCTS UMR CNRS 6638, Limoges, France; F. Basile, I. Bersani, A. Vaccari, University of Bologna, Bologna, Italy; A. Cuni, M. Cornillac, P. Del Gallo, D. Gary, Air Liquide CRCD, Jouy-en-Josas, France

Today, more than 80% of the world hydrogen production is based on Steam Methane Reforming (SMR). This process leads to good yields but also releases huge amounts of CO2. Moreover, it is often run near its working limits, which might cause severe breakdowns on SR units. New reforming processes based on renewable resources, such as Ethanol Steam Reforming (ESR), are developed to compete with SMR. Moreover re-considering the catalytic bed can help in challenging the current industrial issues (pressure drop, thermal transfer limitations, loss of catalytic activity). Our study is focused on the elaboration of supported catalysts for steam reforming processes (ESR and SMR). Supported catalysts with controlled macrostructure (shape, porosity) and microstructure (size and dispersion of catalytic active sites) are currently developed. Ceramic foams are used as catalyst supports. They are processed by slurry-impregnation of sponge-like sacrificial templates. Alumina foams obtained can then be coated either with sol or with slurries, and metal precursors are then impregnated on coated foams. As-prepared catalysts undergo ageing treatments with limited degradation of their macro/microstructures. Such designed catalysts are demonstrated to be interesting materials for SR processes.

Session CF-4

Materials for Electrochemistry and Electrochemical Energy Conversion and Storage

CF-4.1 Ionic, Mixed and Electronic Conductors

CF-4.1:IL01 **Advances in Novel Ionic Conductors for Electrochemical Applications**

Stephen Skinner*, Ryan Bayliss, Robert Packer, Imperial College London, Department of Materials, London, UK

Alternative oxide materials with complex crystal structures will be discussed as potential routes to high performance, low temperature electrochemical devices. A number of in-situ charactersiation techniques will be described that allow a more detailed understanding of the complex diffusion and redox processes occuring in these complex oxides. Of most interest in this work is our evaluation of interstitial oxide materials and we will demonstrate that fast ion conduction can occur in crystallographically complex materials. From this work we propose a new approach to the development of oxide ion conductors, moving away from the conventional view of isotropic 3D materials as being essential for fast ion conduction.

CF-4.1:IL02 **Modeling, Simulation, and In Situ Characterization of Electrode Materials for Solid Oxide Fuel Cells**

Matt Lynch, Kevin Blinn, Xiaxi Li, Meilin Liu*, Center for Innovative Fuel Cell and Battery Technologies, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA

The demand for clean, secure, and sustainable energy sources has stimulated great interest in fuel cells. One of the grand challenges facing the development of a new generation of fuel cells is the creation of novel electrode materials and unique structures that promote fast transport of ionic and electronic defects, facilitate rapid surface electrochemical reactions, and enhance tolerance to poisoning of contaminants commonly encountered in readily available fuels. This presentation will highlight some recent progress in modeling, simulation, and in situ characterization of electrodes in solid oxide fuel cells, including predictions of electrode reaction mechanisms, modeling of charge and mass transport along surfaces and across interfaces, as well as in situ characterization of surface species and new phases using Raman spectroscopy. Probing and mapping the evolution of surface composition and structure or incipient new phase formation on electrode surfaces relevant to electrode reactions under practical fuel cell operating conditions may provide critical insights into the mechanisms of these reactions, which are vital to achieving rational design of better electrodes, catalysts, and interfaces.

CF-4.1:IL03 **Protons in Ceramics: Effects of the Nanoscale**

Glenn C. Mather*, Domingo Pérez-Coll, Instituto de Cerámica y Vidrio, CSIC, Cantoblanco, Madrid, Spain

Proton transport in the volumetric bulk of ceramics (grain and grain boundary) as the principal electrical conduction mechanism is a relatively unusual phenomenon which may be exploited in electrochemical devices for the production, separation or oxidation of hydrogen. The highest proton conductivities are exhibited by perovskites with basic character in a useful temperature range of 400-800 °C. However, proton conductivity at room temperature via grain boundaries has also been reported recently for several solid-state electrolytes (YSZ, SDC) with nanometric grains. In this communication, we briefly review proton transport in ceramic materials, and report on the electrical properties in humidified and dry conditions of dense $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (nCGO) with grain size, <120 nm, prepared by spark-plasma sintering. Proton transport dominates the electrical conductivity of nCGO in wet atmospheres below 60 °C, as demonstrated by the presence of a conductive H^+/D^+ isotope effect. The pathway for proton conduction via the volumetric bulk or via surface processes is analysed on the basis of the Nernst potentials measured across water-based concentration cells with nCGO membranes and the resistivities of samples in humid atmospheres with blocked and exposed lateral surfaces.

CF-4.1:L04 **Thermo-chemo-mechanical Modelling of Mixed Conductors**

O. Valentin*, E. Blond, Institut PRISME (EA 4229, University of Orléans), Polytech'Orléans, Orléans, France; N. Richet, Air Liquide CRCD, Jouy en Josas, France

For twenty years, the development of MIECs is concentrated on the dense membranes for oxygen separation from air. This pure oxygen source has potential industrial applications in methane reforming reactors for the H2/CO production or in oxycombustion for the CO2 capture from coal power plants. The compromise between the oxygen flux performance, the mechanical reliability and the cost are still a challenge to develop these technologies. This study concerns the macroscopic modelling of the mechanical behaviour taking into account the thermal expansion and the chemical expansion induced by the oxygen diffusion. In previous works, the thermal and chemical expansions have been identified by XRD, dilatometry and TGA[1]. Furthermore, dedicated model and its numerical implementation have been also developed[2]. This work uses the simulation tool developed for studying the relationship between mechanical stresses and oxygen flux. The influence of oxygen bulk diffusion kinetics is discussed regarding to surface exchange one. Then, the impact of operating conditions is discussed.

[1]O. Valentin et al., 11th Conference of the European Ceramic Society, 2009; [2]O. Valentin et al., Comput. Mater. Sci., Volume 46, Issue 4, October 2009, Pages 912-920

CF-4.1:L05 **Thermo-mechanical Characterization of Scandia and Ceria Doped Zirconia- Electrolyte Material for Intermediate Temperature Solid Oxide Fuel Cells**

Wendy Lim, Miladin Radovic, Texas A&M University, USA; Nina Orlovskaya*, University of Central Florida, USA; Thomas Graule, Jakob Kuebler, EMPA Swiss Federal Laboratories for Materials Testing and Research, Switzerland

Thermo-mechanical properties of Scandia and Ceria doped Zirconia (SCZ) - Sc0.1Ce0.01ZrO2 - an electrolyte material for intermediate temperature solid oxide fuel cells has been studied. They include elastic moduli, storage and loss moduli, bending strength and coefficient of thermal expansion. Elastic moduli (Young's and shear moduli) and coefficient of thermal expansion have been studied in 25-900°C temperature range using resonant ultrasound spectroscope (in air) and thermo-mechanical analyzer (in N2) respectively. Storage and loss modulus were determined using dynamic mechanical analyzer in 25-500 °C temperature range in N2 atmosphere while the fracture strength has been determined at room temperature, 300 °C and 600 °C in air using 4-point bending test. The results of 4-point bending have been analyzed using Weibull statistics.

CF-4.1:IL06 **Three-dimensional Measurements of SOFC Electrode Microstructure and Correlation with Electrochemical Performance**

Scott Barnett*, James Wilson, Scott Cronin, Jason Nicholas, Northwestern University, Evanston, IL, USA

Quantitative analysis of electrode microstructure remains a key challenge for connecting materials processing with microstructure and electrode performance. This paper will describe the application of dual-beam focused ion beam - scanning electron microscopy (FIB-SEM) for analyzing electrodes using both stereological analysis of two-dimensional images and reconstruction to obtain three-dimensional images. This analysis yields a number of structural parameters needed for use in electrochemical models, including solid and pore volume fractions, interface areas, tortuosities, and triple-phase boundary lengths. The 3D structure of typical SOFC electrodes - Ni-YSZ and LSM-YSZ (YSZ = Y-stabilized Zirconia; LSM = (La,Sr)MnO3) will be described. A study of the effect of composite electrode composition on structure and polarization resistance will be described. The volume fractions of the electronically-conducting and ionically-conducting phases were varied for both Ni-YSZ anodes and LSM-YSZ cathodes. The influence of the structure of infiltrated cathodes on low-temperature polarization resistance will also be discussed.

CF-4.1:IL07 Migration of Oxide Ions in Ceria Doped with Rare-earth Cations Using First-principles Density Functional Study

M. Nakayama[1, 2]*, M. Martin[2], [1]Dept. of Materials Science and Eng., Nagoya Institute of Technology, Nagoya, Aichi, Japan, [2]Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

Oxygen transport in rare-earth oxide (RE2O3) doped CeO2 with fluorite structure has attracted considerable attention owing to both the range of practical usage and the fundamental fascination of fast oxide ion transport in crystalline solids. Using density-functional theory, we have calculated the formation energies of point defects and their migration properties in CeO2 doped with various RE2O3. The results show oxygen vacancy form associates with the RE3+ ions, and the corresponding defect association energy is a strong function of the ionic radii of the RE3+ dopants. Nudged elastic band methods are adopted to study the migration of an oxide ion. The migration energy of an oxide ion also strongly depends on the ionic radii of the neighbouring dopant cations. Accordingly, we have identified two factors that affect the oxygen vacancy migration; (1) trapping (or repelling) of an oxygen vacancy at the NN site of the RE3+ dopant, and (2) reduction (or enlargement) of the migration barrier by RE3+ doping. These findings provide insight for atomistic level understanding of ionic conductivity in doped ceria and would be beneficial to optimize ionic conductivity.

CF-4.1:IL08 Applications of Mixed Conducting Protection Layers in High Temperature Electrochemical Devices

Z. Gary Yang, Pacific Northwest National Laboratory, Richland, WA, USA

For satisfactory performance, electrochemical energy conversion and storage systems, such as solid oxide fuel cells and Na-beta alumina batteries, respectively, require operation at relative high temperatures. One major challenge to the high temperature devices is the durability of components, in particular, made from metallic materials. These components are typically applied with protective oxide coating to protect them from environment attack for a satisfactory durability. Unlike tradition protective coatings, however, they have to be electronically conductive in the electrochemical devices. One typical example is the metallic interconnect in solid oxide fuel cells and other electrochemical conversion and storage systems. A systematic work has been carried out at US-DOE Pacific Northwest National Lab on the protective layers on metallic (e.g. stainless steel) interconnects. Mixed conductors, such as (Mn,Co)3O4 spinels and varied perovskite compositions, were investigated for the particular purpose. Novel approaches were developed to apply the oxide protection layers. Both short and long term tests were carried out to evaluate their durability and electrochemical properties in operating conditions. The paper will reprot details of the work and discuss the status and challenges of this particular area.

CF-4.1:L09 Constrained and Non-constrained Sintering of Plasma-sprayed Zirconia Based Electrolytes for SOFCs

C. Christenn*, A. Ansar, DLR, Institute of Technical Thermodynamics, Stuttgart, Germany

The current development in SOFCs is focused on reducing the operating temperature below 800 °C. The reduced operating temperature promotes durability of cells and decreases stringent demands on peripheral components. However, with lower temperature the ionic conductivity of electrolytes decreases. Thickness reduction of the conventionally used yttria-stabilized zirconia electrolyte by using nanostructured particles as feedstock is a possibility to avoid this problem. Another possibility is the use of an electrolyte with improved ionic conductivity for intermediate temperature SOFCs, e.g. scandia-stabilized zirconia. Within this work zirconia based electrolyte layers were deposited on metal substrates using plasma spraying. As all thermal sprayed coatings contain some porosity, which influences the cell performance, the sprayed electrolyte layers were sintered in a second step. Plasma-sprayed coatings were under compressive stresses. In order to achieve a better understanding of differences in the sintering behaviour, plasma sprayed layers were sintered under constrained and non-constrained conditions in the temperature range of 800 to 1520 °C and characterised. Sintering properties, microstructure, and conductivity of sprayed and sintered electrolyte layers were investigated.

CF-4.2 Energy Conversion and Storage

CF-4.2:IL01 Towards the Miniaturization of Solid Oxide Fuel Cells

Enrico Traversa, International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan

The development of micro-solid oxide fuel cells (SOFCs) opens new scenarios for portable unit power generation. Micro-SOFCs are likely to produce energy densities per volume and specific energy per weight up to four times larger than state-of-the-art batteries. Reducing the operation temperature is critical for practical use of miniaturized SOFCs and can be achieved using thin-film electrolytes and engineering suitably micro-structured electrodes. Pulsed laser deposition (PLD) is very promising for the fabrication of tailored oxide thin films, because it allows obtaining single crystal or polycrystalline films, with tailored microstructure from dense to highly porous. This talk shows examples of PLD fabricated SOFC components and their assembly, such as dense epitaxial oxygen ion (ceria) and protonic (barium zirconate) electrolyte films in single crystal and polycrystalline forms. Bilayer electrolyte structures were also fabricated to improve performance. Dense electrolyte films coupled with micro-structured porous cathode layers were grown on porous sintered substrates for the fabrication of anode supported SOFCs.

CF-4.2:IL03 Single-phase vs. Two-phase Mechanism of Li+ Extraction from LiFePO4: the Role of Defects

C. Masquelier*, S. Hamelet, P. Gibot, M. Casas Cabanas, J.M. Tarascon, LRCS Amiens; C. Grey, J. Cabana, Stony Brook NY; S. Levasseur, P. Carlach, Umicore, Belgium

Low temperature routes (precipitation in aqueous medium) used to produce small particles (~50 nm to 100 nm) of LiFePO4-type powders result in LixFeyPO4 compositions with significant amounts of structural defects (Li/Fe antisites) which show unusual voltage profiles vs. composition (sloping voltage) when used as positive electrodes in Li batteries. The reactivity in air at moderate temperatures of these powders was investigated in much details and led to the discovery of significant Fe mobility, resulting in even higher concentrations of structural defects. Completely new electrochemical mechanisms were spotted through in situ X-ray diffraction, NMR, X-ray absorption and Mossbauer spectroscopy.

CF-4.2:L05 Flexible SOFC: Challenges

Hyoup Je Cho, Gyeong Man Choi*, Department of Materials Science and Engineering/ Fuel Cell Research Center, Pohang University of Science and Technology (POSTECH), Pohang, Korea; Young Min Park, Fuel Cell Project, Research Institute of Industrial Science and Technology, Pohang, Korea

SOFC (Solid Oxide Fuel Cell) has advantages in efficiency, power density, life time and multifuel capability. However, SOFC is very weak against mechanical or thermal shock due to its inherent brittleness and the low thermal conductivity of the component materials. SOFC is commonly manufactured either in the form of electrolyte-supported or anode-supported type. However, metal-supported SOFC is more promising due to its mechanical strength, thermal shock resistance, and low cost etc.. The high mechanical and thermal strength of the supporting metal compensates the weakness of ceramics and thus strengthens the cell. In this study, we have developed a thin (<~250µm) metal-supported SOFC using a simple and common co-sintering process. The strong and thin structure gives flexible nature to SOFC. In the presentation, we will discuss the fabrication technique and electrochemical performance. The performance is comparable to or better than the conventional electrolyte- or anode-supported SOFC.

CF-4.2:IL06 Mathematical Modeling of Electrochemical Systems. Application to Li-ion Batteries Aging

M. Safari[1, 2], M. Morcrette[1], A. Teyssot[2], C. Delacourt[1]*, [1]Laboratoire de Réactivité et Chimie des Solides, Université de Picardie Jules Verne, Amiens, France; [2]Renault Research Department, Guyancourt, France

Aging of Li-ion batteries is becoming more and more a concern because of their potential use for electric transportation, for which lifetimes of 10 and 15 years are targeted for EVs and HEVs, respectively. This emphasizes the need for effective life-prediction methods. In this talk, we will present our recent work on various modeling approaches for predicting the life of a Li-ion battery. While physics-based models require an extensive understanding of the underlying chemistry and aging phenomena, the battery performance upon aging under various modes of operation / usage profiles is readily simulated. This will be exemplified with a model of solid-electrolyte interphase growth on the anode particles, used for the analysis of aging data under cycling and storage. On the contrary with physics-based models, empirical approaches do not require a detailed knowledge of the aging phenomena, but their prediction capability is questioned. An empirical approach, based on an analogy with mechanical fatigue, will be presented. The physics-based model previously detailed is used as a surrogate battery i) for generating dummy aging data used for the empirical correlations and ii) for an assessment of the prediction capability of this fatigue-based approach under various usage profiles.

CF-4.2:IL07 **Cathode Materials for Large-scale Lithium-ion Batteries**

Atsuo Yamada, Department of Chemical System Engineering, The University of Tokyo, Tokyo, Japan

Our recent studies on oxyanion compounds as cathode materials for large scale lithium batteries will be reviewed. Crystalline size has tremendous effect to the thermodynamics and kinetics in intercalation compounds. In LixFePO4, the phase changes by simple two-phase separation but with controllable miscible character by raising temperature and/or reducing crystalline size, thereby provides simple model system to rationalize thermodynamics and electrochemistry in electrode reaction. With respect to the phase diagram and thermal excitation of lithium in LixFePO4, we applied the maximum entropy method to neutron diffraction data for Li0.6FePO4 at 620 K, and successfully visualized the one-dimensional curved lithium diffusion path in LixFePO4. Under this experimental condition, lithium only is in the dynamic situation where the FePO4 framework remains to be rigid. This provides the long-awaited experimental evidence for such strong dimensional restriction of lithium motion in LixFePO4. Beyond LixFePO4, this is the first visual demonstration of the ion diffusion path in a battery electrode. Structural determination of the emerging promising compounds, Li2MSiO4. as well as exploration of compounds with the lightest small triangle oxyanion, (BO3)3- will be intoduced as time permits.

CF-4.2:L08 **YSZ Self-supported Ultrathin Membranes for µSOFCs**

J. Santiso[1]*, A. Tarancón[2], I. Garbayo[2], A. Cavallaro[1], J. Roqueta[1], G. Garcia[3], I. Gràcia[2], C. Cané[2], N. Sabaté[2], [1]CIN2, Research Center for Nanoscience and Nanotechnology, CSIC-ICN, Campus UAB, Bellaterra, Barcelona, Spain; [2]CNM-IMB (CSIC), National Institute of Microelectronics, CSIC, Campus UAB, Bellaterra, Barcelona, Spain; [3]GFMI, Dept. of Physics, Autonomous University of Barcelona, Campus UAB, Bellaterra, Barcelona, Spain

Some recent developments in the fabrication of microSOFCs from self-supported membranes have demonstrated the potential use of these fuel cells in the low power regime (1-20W) at moderate temperatures (400-500 °C). However, there are still some limitations in the development of larger, more efficient and durable devices related to the thermomechanical stability of the membranes and their electrochemical performance. In this work we present a study of the residual stresses measured on YSZ electrolyte membranes obtained under different conditions and geometries, and their electrical behaviour at operating temperatures. Self-supported YSZ membranes were fabricated from pulsed laser deposited thin films on patterned Si3N4 membranes on Si/SiO2 substrates, and subsequent removal of underlying Si3N4 by dry etching. The deposition process was optimized to obtain crystalline, dense and homogeneous films for a thickness from 60 to 240nm and surface areas between 420x420 µm2 and 820x820 µm2. Residual stress was measured by different techniques and showed important variations from compressive to tensile strain. Electrical characterization along transverse direction showed a bulk behavior, and ASR target value of 0.15?cm2 is achieved at temperatures as low as 425 °C for YSZ membranes of 240nm.

CF-4.2:L09 **Thick Film and Multilayer Ceramic Technology for Innovative Fuel Cell Systems**

A. Michaelis, Fraunhofer Institute for Ceramic Technologies and Systems, IKTS, Dresden, Germany

Due to their broad spectra of favourable properties high performance ceramic materials offer enormous potential for product innovation in the field of energy conversion. The joint application of structural and functional ceramic technology allows for unique combination of electronic, ionic (electrochemical) and mechanical properties enabling for development of new highly integrated micro- mechanical systems (MEMS). For this, we apply hybrid and multi layer ceramic technologies such as LTCC (low temperature cofired ceramics) and HTCC (high temperature cofired ceramics). We present a new fully integrated PEM (polymer electrolyte membrane) fuel cell system completely manufactured in LTCC technology. A big advantage of LTCC technology is its compatibility with conventional Si-microelectronic and piezo-components allowing for a direct integration of such devices in the electrochemical fuel cell microsystems. For higher power applications in the kW range ceramic SOFC (solid oxide fuel cell) systems are favourable. We apply HTCC related technology for their production. Examples for fabrication of robust electrochemical MEA (membrane electrode assemblies), glass seals and contact interlayers are given.

CF-4.2:L10 **Progress in the Development of Bulk-type All Solid State Lithium Batteries**

V. Viallet*, V. Seznec, M. Morcrette, J.M. Tarascon, LRCS UPJV, Amiens, France; G. Delaizir, P. Rozier, M. Dolle, Cemes, Toulouse, France; A. Aboulaich, L. Tortet, R. Bouchet, LCP, Marseille, France

Owing to safety concerns dealing with liquid-based Li-ion batteries, efforts are being pursued to realize bulk-type solid-state cells offering higher energy densities than thin films. Among others, Hayashi et al. recently reported very encouraging performances for Li-ion cells based on sulphide-based solid electrolytes, with inherent drawbacks linked to the need of cold pressing thin electrodes with limited amounts of active materials. Nowadays, the development of bulk-type solid batteries appears to be limited by the difficulty in assembling dense laminated materials, which requires careful optimization of sintering processes. Our approach is to develop bulk-type all solid state batteries by means of an emerging powder consolidation process: Spark Plasma Sintering (SPS). In such technique, the heat generated internally by a pulsed DC current directly passing through the conducting die may greatly favour high quality contacts between the different active parts of an all-solid state battery, in very short times and at low cost. Promising achievements in terms of practical capacity delivered, overall reversibility and cycling stability will be presented as well as our strategy in choosing the appropriate materials and the different steps of the development of bulk-type batteries.

CF-4.2:IL11 **Three Dimensionally Ordered Composite Electrodes with Active Oxide Material and Ceramic Electrolyte for All Solid State Rechargeable Lithium Battery**

Kiyoshi Kanamura, Department of Applied Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo, Japan

All solid state rechargeable lithium ion battery has been paid much attention as new category of electrochemical energy storage device. In this battery, lithium ion conductive ceramics have been used to construct rechargeable lithium battery. The most important technology is a creation of large electrochemical interface between solid electrolyte and active material. In order to create well-established interface using solid electrolyte, three dimensionally ordered macroporous solid electrolyte with high lithium ion conductivity was prepared. The template consisting of mono-dispersed polystyrene beads was utilized to a preparation of 3DOM electrolyte. The size of pore in 3DOM electrolyte was 1 µm. This porous electrolyte consisted of macropores connected by small holes. An active material, such as Lithium cobalt oxide was injected into all macropores, which provided a large interface area between active material and solid electrolyte. The injection of active material was used as sol-gel process combined with vacuum impregnation followed by heat treatment. From SEM observation, a good contact between active material and solid electrolyte was convinced. Electrochemical performance of this compositesystem was tested. The electrochemical impedance was extremely reduced.

CF-4.2:IL12 **Micro-solid Oxide Fuel Cells: From Thin Films to Power Delivering Membranes**

Jennifer L.M. Rupp*, Anja Bieberle-Hütter, Ludwig J. Gauckler, ETH Zurich, Zurich, Switzerland

Micro-Solid Oxide Fuel Cell (µ-SOFC) membranes integrated on micromachinable substrates such as silicon wafers have potential for battery replacement and power supply of portable electronics such as laptops, mobile phones or PDA's. Compared to state-of-the-art solid oxide fuel cells µ-SOFCs exhibit by two orders of magnitude reduced cell thickness and allow, thus, for low temperature operation below 550 °C with reasonable power output. Recently, first µ-SOFC membranes of 200 µm and less than 1 µm in total cell thickness were integrated on micromachinable silicon and Foturan glass-ceramic wafers[1, 2]. In the present paper we would like to show different strategies to manufacture micro-Solid Oxide Fuel Cell. For this, three different micro-Solid Oxide Fuel Cell designs based either on the microfabricationable substrates silicon or Foturan, or on a nanoporous support structure will be presented. The relevance of thin film microstructures on the power performance of micro-Solid Oxide Fuel Cell membranes will be discussed.

[1]Huang, et al, J. Electrochem. Soc., 2007; [2]Muecke, et al, Adv. Mater., 2008

CF-4.3 Materials for Electrochemistry

CF-4.3:IL01 Semiconducting Oxide Electrodes for Photoelectrochemical Water Splitting

Avner Rothschild, Dept. of Materials Engineering, Technion - Israel Institute of Technology, Haifa, Israel

Photoelectrochemical splitting of water using solar energy has great potential for clean production of hydrogen fuel using renewable and abundant resources - water and sunlight. However, despite intense research efforts since the early 70's, stable and efficient photoelectrodes have not been discovered yet. While conventional semiconductors such as Si and GaAs photo-corrode in aqueous electrolytes wide band gap semiconducting oxides such as TiO2, WO3, and Fe2O3 are stable and therefore they make a better choice for PEC cells. But their light absorption and charge transport properties are substantially poorer compared to conventional semiconductors. Consequently, their photon to chemical energy conversion efficiency is rather small. The highest efficiency level was reported by Grätzel in 2006 using silicon-doped a-Fe2O3 (Hematite) nanostructured electrodes prepared by atmospheric pressure CVD. In this paper I present our work on oxide photoelectrodes for water splitting. We study the fundamental processes involved in the photoelectrochemical water splitting reaction using model thin film electrodes with precisely controlled microstructure and chemical composition. Our goal is to understand the limiting factors and the correlation between material properties and cell performance.

CF-4.3:IL02 Photocatalytic Activity of Ceramic Foam Supported TiO2, TiO2/Ce and TiO2/Zr Thick Films

G. Plesch*, M. Vargová, K. Jesenák, Faculty of Natural Sciences, Comenius University, Bratislava, Slovak Republic; U.F. Vogt, M. Gorbár, Empa, Swiss Federal Laboratories for Materials Testing and Research, Dübendorf, Switzerland; T. Mancino, P. Colombo, Università di Padova, Padova, Italy

Recently much interest has been devoted to study of photocatalytic properties on titania since TiO2 has unique performance for photoactivated degradation of various contaminants. It is highly advantageous to immobilize the nanocrystalline TiO2 powder catalyst on an appropriate support. The open three dimensional reticulated structure of macroporous ceramic foams is capable of homogenizing non-uniform flows, which makes them highly suitable as catalyst support. This contribution is devoted to studies on TiO2 thick films deposited on ceramic reticulated foam substrates with pore sizes of 10 and 15 ppi. Commercial Aeroxide® P25, TiO2 powders synthesized by coprecipitation and TiO2 powders doped with Ce(IV) and Zr(IV) were deposited on macroporous foams by dip-coating and subsequently annealed up to 700 °C. Coatings with a thickness up to 20 um were obtained. The photomineralisation of phenol in aqueous solutions catalyzed by TiO2 films was investigated by determination of total organic carbon (TOC). The relations between chemical composition, microstructure and photocatalytic activity will be discussed.

This work was supported by the Scientific Grant Agency of the Slovak Republic VEGA and the Slovak Research and Development Agency (project APVV-VVCE-003307)

CF-4.3:L03 Analysis of Degradation and Aging Processes in Solid Oxide Electrolyser Cells

Ulrich F. Vogt*, Daniel Wiedenmann, Lorenz Holzer, Andreas Züttel, Empa Materials Science and Technology, Dübendorf, Switzerland; Anne Hauch, National Laboratory for Sustainable Energy, Risoe, Technical University of Denmark, Roskilde, Denmark

Solid Oxide Electrolyser Cells (SOEC), have a great potential for a cost efficient and economical production of hydrogen by water electrolysis. The electricity demand for water splitting can be significantly reduced if the formation of hydrogen takes place at temperatures between 600 to 900°C. At these temperatures, the required electrical energy can be partially substituted by thermal energy, as the process is increasingly endothermic with rising temperature. If steam is available from solar, nuclear or geothermal sources, the production cost of hydrogen can even be reduced significantly. The elevated operation temperatures can lead to material degradation and aging processes and thus influencing the SOEC performance. The precipitation of impurities (cell-poisoning), element diffusion, grain coarsening, as well as delamination of cell parts due to inhomogeneous thermal expansion can lead to a loss of efficiency or even the failure of the cell. Chemical and structural characterization were performed by electron-probe microanalysis (EPMA) at the micro-scale level over a large sample area and for selected samples at the nano-scale level by combining focused ion beam technique (FIB) and transmission electron microscopy (TEM).

CF-4.3:L05 Development of Porous ZrO2 Diaphragms for Alkaline Electrolysis

M. Gorbar*, U. Vogt, V. Herzog, D. Wiedenmann, A. Züttel, Empa Abt. 138 "Hydrogen & Energy", Dübendorf, Switzerland

Hydrogen energy is becoming increasingly important in the recent technological progress. High purity hydrogen production via electrolysis of water from alkaline aqueous electrolyte is a well-established technology. Conventional alkaline electrolysers with zero-gap cell geometry operate at 85 °C, 32 bars and use 25 wt% KOH solution as electrolyte. The electrodes are separated by gas-tight, but ion-permeable diaphragm, which forms an efficient barrier for the gas molecules and prevents their unhindered intermixing. Traditionally used asbestos diaphragms, have to be replaced due to health regulations, therefore we focused our work on preparation of ceramic porous substrates, in order to find alternatives to asbestos. The mixtures of powder ZrO2 - C were uniaxialy pressed to the cylindrical preforms and subsequently sintered. By using different amounts of carbon, the effects on the open porosity were examined. The all substrates were tested in lab-electrolytic cell at ambient conditions, in order to provide a basis for development of new diaphragms. These tests characterised the gas purity, gas flow and voltage drop of made zirconia substrates.

CF-4.3:L06 Photocatalytic Efficiency of ZnO/TiO2 Composite Plates in Degradation of RR180 Dye Solutions

M. Konyar[1]*, D. Ovali[1], H.C. Yatmaz[2], C. Duran[1], K. Öztürk[1], [1]Gebze Inst. of Technology, Materials Science & Engineering Dept., Cayirova Campus Gebze, Kocaeli, Turkey; [2]Gebze Institute of Technology, Environmental Engineering Dept., Muallimkoy Campus Gebze, Kocaeli, Turkey

The tape casting method was used to prepare ZnO/TiO2 composite plates for photocatalytic degradation of Reactive Red 180 (RR 180) textile dyes in aqueous solutions. The TiO2 content of the plates was selected as 20 mol%. The final sintering temperature of the plates is 700 °C. The relatively low sintering temperature of 700 °C was selected to obtain relatively high surface area plates which enhances the photocatalytic activity in the degradation processes. The plates were characterized by using TG-DTA, BET, XRD and SEM. The efficiencies of the composite plates during the degradation of the RR180 dye were determined using the laboratory-scale quartz photoreactor under UVA-light irradiation. Up to 85% color removal was obtained in 90 minutes for the RR180 dye solution at 50 mg/lt concentration. In our previous investigation, the pure ZnO plates sintered at the same temperature yielded only 50% color removal efficiency for the same dye solution in 90 minutes. The addition of TiO2 is found to increase the photocatalytic activity of the ZnO plates in degradation of the selected dye from water.

CF-4.3:L07 Chemical Etching of Advanced Ceramics

H.T. Ting*, School of Eng. & Science, Curtin University of Technology, Miri, Malaysia; K.A. Abou-El-Hossein, Dept. of Mechanical & Aeronautical Eng., University of Pretoria, Pretoria, South Africa; H.B. Chua, School of Eng. & Science, Curtin University of Technology, Miri, Malaysia

The present thesis discusses the development of the first and second order models for predicting the chemical etching variables such as etching rate, surface roughness and accuracy of advanced ceramics. The first and second order etching rate, surface roughness and accuracy equations were developed using the response surface method (RSM). The cutting variables were the etching temperature, etching duration, etching solution and solution concentration. The predictive models analyses were supported with the aid of the statistical software package Design Expert 7.0 (DE 7). The effects of individual input cutting variables and the interaction between these variables were also studied. The study found that the predictive models able to predict the etching rate, surface roughness and accuracy to those reading recorded experimentally with a 95% confident interval. The results obtained from the predictive models were also compared by using multilayer perceptron artificial neural network. chemical etching parameters predicted by using Neural Network were in good agreement with that obtained by RSM. This observation indicates the potential of using artificial intelligence in predicting chemical etching parameters thus eliminating the need for exhaustive chemical etching in optimization.

Poster Presentations

CF:P01 Study of Tungsten Oxide Nanostructured Films for Gas Micro Concentrations Measurements

O.M. Ivanova*, A.E. Tarasova, S.A. Krutovertsev, A.V. Pislyakov, A.V. Shevchenko, JSC "Practic-NC", Zelenograd, Moscow, Russia

Recently large interest appeared to the study of WO3 possibility to detect gas components in atmosphere. Tungsten oxide is well known as electrochromic material. But, its sensing properties were investigated not yet fully. This paper presents comparative sensor temperature characteristics of WO3 thin and thick films. The sensitive element consists of an alumina 2 x 0.5 x 0.2 mm substrate. One side of the substrate is covered with a gas sensitive film; the other side of the substrate is platinum film heater. It is the thermal resistor of the sensor. Sensitive layers were formed by two methods: thick film technology and thermal sputtering in vacuum. The investigations were carried out under the sensor thermal stabilization conditions in the range 100 - 450 °C. Sensor heating, conductivity and resistance measurements were maintained by specially developed unit and IBM PC program which operates in real time conditions. All films are mostly sensitive to the relative humidity when it is less than 30% at temperatures which are less than 200 °C. Both type films show maximal sensitivity at 150 °C to NO2 micro concentrations. Thick films resistance increases five times at NO2 concentration of 5 ppb. Films sensitivity to the H2S micro concentrations at 25-350 °C was investigated. The maximal resistance change at 5 ppb of H2S is observed at 300-350 °C. The sensor film characteristics can be purposely changed by varying conditions of film formation and by varying film temperature at which measurements are performed.

CF:P02 **Development of Noninvasive Diagnosis with Semiconductor Sensors**

S.A. Krutovertsev*, M.V. Chuprin, O.M. Ivanova, A.V. Pislyakov, A.V. Shevchenko, JSC "Practic-NC", Zelenograd, Moscow, Russia; V.V. Kalinovsky, V.V. Konovalov, VNIIEF, Sarov, Nizhniy Novgorod Region, Russia

In the present time, health control for illness detection on the early stages has acquired important meaning. One direct and reliable noninvasive method of monitoring states of allergic inflammation in the upper respiratory tracks of patients suffering from bronchial asthma can be based on defining the concentrations of NO in the exhaled air. This work is developing the problem solution of early noninvasive diagnosis. This task can be solved by using methods based on semiconductor films for gas control. The characteristics of the new sensors, developed on the basis of ZnO, WO3 and SnO2 and intended for NO as inflammation marker defining in breath, have been investigated. The sensitive element consists of an alumina 2 x 0.5 x 0.2 mm substrate. One side of the substrate is covered with a gas sensitive film using thick-film technology; the other side of the substrate bears a film heater made of platinum paste. The film heater is, at the same time, the thermal resistor in the sensor. The investigations were carried out under the sensor thermal stabilization conditions in the range 50-450 °C. Sensors showed the best sensitivity to NO at temperature of 150 °C. A temperature impulse mode effect on a sensitive layer was used for the model gas mixtures and breath analysis. Sensors based on ZnO had high repeatability and stability of gas sensitivity. Sensitivity to nitric oxide was 10 ppb. The influence of other gases present in exhaled air at working temperature can be estimated by mathematical processing.

CF:P03 **Characterization of a Flexible Ceramic Membrane and the Effect of its Chemical Modification on the Transport of Ions**

R. de Lara[1], L. Pelález[1], D. Toledo[1], F.J. Casado[2], J. Hierrezuelo[2], J.M. López-Romero[2], J. Benavente[1]*, [1]Grupo de Caracterización Electrocinética en Membranas e Interfases, Departamento Física Aplicada I, Universidad de Málaga, Málaga, Spain; [2]Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Málaga, Málaga, Spain

A planar and flexible commercial composite ceramic membrane (Al2O3/ZrO2 particles supported on a stein steel network by Degussa) was hydraulic and electrically characterized by different kinds of experiments (volume flow-pressure relationships, impedance spectroscopy, streaming and membrane potential) carried out with the membrane in contact with NaCl solutions at different concentrations. These measurements allow the determination of characteristic parameter such as hydrodynamic permeability, electrical resistance, zeta potential and ion transport numbers, which give information on the electropositive character and morphology of the composite membrane. Chemical modification of the membrane was performed by immersion in a decaethyleneglycol mono-ethylether aqueous solution (5% w/v). Surface and bulk membrane changes were determined by comparing X-ray photoelectron spectroscopy (XPS) spectra and membrane potentials for original and modified samples. These results show the presence of the modifying substance on the membrane surface but also into the composite structure by causing an increase in the transport of cations across the membrane, which indicates a reduction in the electropositive character of the Al2O3/ZrO2 original membrane.

CF:P04 **Determination of Lead Traces by Stripping Voltammetry Using Ti(N,C) Working Electrodes**

M. Ziemnicka*, B. Bas, M. Je, L. Stobierski, Faculty of Materials Science and Ceramics, AGH Univ. of Science and Technology, Kraków, Poland

Electrochemical stripping techniques still attract considerable attention for trace metal analysis and for measuring several important organic compounds, due to their unique capabilities of pre-concentrating the analytes at the electrode surface and associated favorable low limits of detection. In this work it is reported for the first time that the Ti(N0,1C0,9), Ti(N0,4C0,6) and Ti(N0,5C0,5) working disc electrodes, a "mercury-free" sensors, offer surprisingly good analytical performance and some valuable properties. The analytical applicability of the Ti(N,C) electrode was confirmed in determination of lead(II) traces in synthetic solutions with and without surfactants, in certified reference material and in natural water samples. The effects of dissolved oxygen, acids, anions and metal ions were investigated for the Ti(N,C) electrode. Newly prepared and not activated electrode cannot be polarized. Therefore, to use the electrode as a voltammetric sensor, its electrochemical activation is required. Composition of conditioning electrolyte and procedures of the electrodes activation were optimized. The fabrication and the response performance of the investigated electrodes were described in the paper. The voltammetric data were associated with the structural characterization of the electrode surface using scanning electron microscopy (SEM) and transmition electron microscopy (TEM).

CF:P05 **Solid Oxide Electrolyte Based Oxygen Pump**

A.V. Spirin*, A.S. Lipilin, V.V. Ivanov, S.N. Paranin, A.V. Nikonov, V.R. Khrustov, D.S. Portnov, N.V. Gavrilov, A.S. Mamaev, Institute of Electrophysics, Russian Academy of Sciences, Ekaterinburg, Russia

The prototype of high temperature electrochemical oxygen generator (pump), e.g., for medical applications has been developed and fabricated. It is based on thin-walled (100-150 microns) tubular segments of solid oxide YSZ electrolyte with LSM electrodes. Assembled electrochemical cell consists of several segments jointed and connected in series with the use of non-precious metallic elements. The different technologies: nanopowders production by laser ablation, casting of polymer-ceramic tapes, formation of tubular electrodes-electrolyte green structures by radial magnetic pulsed compaction of proper tapes, were used for the segments fabrication. The usage of nanopowders permitted to lower sintering temperature down to 1200 °C and to realize co-sintering the YSZ and LSM functional layers. The interconnects were made up of heat-resistant steel with protective coating applied by magnetron sputtering method. The productivity of the presented oxygen generator prototype was 9 l/h at the temperature of 800 °C and current density of 1.1 A/cm2. The surface area of the electrodes was 32 cm2. The power inputs on electrochemical parts for producing one cubic meter of oxygen come to 6 kW*h. Produced oxygen has near 100% purity and sterility.

CF:P06 **Oxygen Permeability and Methane Conversion Rate Properties of the LaxSr1-xTi1-yFeyO3-δ Perovskite type Membrane**

Eun Jeong Yi[1]*, Hae Jin Hwang[1], Ji-Woong Moon[2], [1]Division of Material Science and Engineering, Inha University., Incheon, Korea; [2]Research Institute of Industrial Science & Technology, Pohang, Korea

A dense mixed ionic and electronic conducting ceramic membrane is one of the most promising materials for oxygen separation from a gas mixture, a syngas synthesis via CH4 partial oxidation and so on. The ABO3 perovskite structure, SrTiO3 shows high chemical stability at high temperatures under reduction and oxidation atmospheres. Its low electronic and ionic conductivities was improved by doping La3+ as donors on Sr2+ site and doping Fe3+ as an acceptor on Ti4+ site. In this study, La and Fe co-doped SrTiO3 was synthesized via solid state reaction. LaxSr1-xTi1-yFeyO3-d membranes were fabricated by sintering green compacts at 1250 to 1400 °C for 5 hrs. XRD analysis showed that there was no phase change after heat-treating the samples under reduction and oxidation conditions. Membranes were found to be a good electrical conductor and electrical conductivity increased with increasing Fe content. Oxygen permeability and methane particle oxidation rate of the membranes were characterized by using micro gas chromatography (micro GC) under Air-5%CH4/Ar. Thermal stability of the perovskite phases in air atmospheres was demonstrated by TG/DTA and Dilatometer.

CF:P07 **Development of Ultrasonic-optical Fiber Hydrogen Sensor**

Jung-Cheol Yoo*, Tai-Hong Cheng, Il-Kwon Oh, School of Mechanical Systems Engineering, Chonnam National University, Gwang-Ju, Korea

In this study the ultrasonic-optical fiber hydrogen sensor was newly developed for monitoring the pressure of a hydrogen gas tank and detecting the hydrogen leakages. Previously we developed the pitcher-catcher and the pulse-echo sensor system for health monitoring of structure. In the pitcher-catcher sensor system the ultrasonic wave generated from a piezoelectric actuator is guided and propagated through the optical fiber and subsequently sensed by a piezoelectric sensor. For detection of hydrogen the optical fiber is coated with palladium particles which expand on exposure to hydrogen. Palladium is chosen because, when exposed to hydrogen, they adsorb hydrogen gas and swell slightly to form palladium hydride. The change in palladium dimensions affects the wave propagation impedance of optical fiber for detecting the hydrogen gas, and this method has been applied in both the pitcher-catcher sensor and the pulse-echo sensor systems. Our results showed that the ultrasonic-optical fiber hydrogen sensor system can be successfully employed for hydrogen detecting system. By using pitcher-catcher hydrogen pressure sensor system the pressure of hydrogen tank can also be monitored. Also the exact location of hydrogen leakage can be detected using pulse-echo hydrogen sensor system.

CF:P09 **Understanding ac Response of Proton Conducting Perovskites**

Jong-Sook Lee, Yong Kim*, Eui-Chol Shin, Chonnam National University, Gwangju, Korea; Jong-Sung Park, Yu-Eun Park, Byung-Kook Kim, Korea Institute of Science and Technology, Seoul, Korea

Although impedance spectroscopy has been widely employed to characterize the transport properties of ceramic proton conduction in perovskites, this class of material characteristically exhibits severe overlapping impedance responses and large polarization at low frequency range, which is critical for practical applications, but still obscure. While the bulk conductivity at high temperature above 500 °C is affected by the mixed conduction, significant defect interactions are expected to occur in these highly doped materials at low temperature. In the present work the ac response of the representative proton conducting perovskites, 15 m/o yttria doped barium zirconate and cerate, was comparatively investigated to address these key issues.

CF:P10 **Thermoelectric Properties of Sr-doped RECoO3 (RE=Pr,Sm)**

T. Ohtani*, K. Minami, Okayama University of Science, Okayama, Japan

Sr-doped RECoO3 (RE=Pr,Sm) with perovskite-type structure was prepapred by heating the mixtures of RE oxides, Co carbonate, and Sr oxalate. Electrical resistivity and Seebeck coefficients were measured from 100 to 1100K. It was found that the values of electrical resistivity decrease with increasing Sr contents. Both oxides showed a metal-to-semiconductor transition at about 870K. The most remarkable is that the dominant carriers were changed from holes to electrons with lowering temperature at ca. 300K These oxides showed the relative large values of power factor for both p-and n-type conduction regions.

CF:P11 **Creep and Fracture of Proton-conducting Perovskite Oxides**

C. Vaquero-Aguilar, M. Jiménez-Melendo*, Dpto. de Física de la Materia Condensada, Universidad de Sevilla, Sevilla, Spain

In the last years, high temperature proton conductors have received much attention due to their potential applicability to a broad range of electrochemical applications: steam electrolysers, solid state fuel cells, gas separation membranes, high-density energy storage applications, etc. Although many studies have addressed the processing, structure, defect chemistry and conductivity of doped perovskites, only a few studies have focused on their plastic behavior, which is essential for ultimate component performance, as well as for sintering and grain growth. In this study, Y- and Yb-doped BaCO3 polycrystals were fabricated from commercial powders by solid-state reaction and subsequent sintering. The resulting microstructures have been studied by scanning and transmission electron microscopy, energy-dispersive X-ray spectrometry and X-ray diffraction. The samples exhibit an uniform and equiaxed microstructure with grain sizes below 1 micrometer. The mechanical properties have been studied in compression up to 1300 °C in air at constant strain rate and under constant load. Mechanical data and microstructural observations are correlated with dopant type and content, in order to identify the fracture and deformation controlling mechanisms.

CF:P13 **Synthesis and Characterization of LiMnP1-xVxO4-delta Solid Solutions**

D. Kellerman*, Institute of Solid State Chemistry, Urals Div. RAS, Ekaterinburg, Russia; N. Mukhina, V. Gorshkov, B. Tsarev, OOO Eliont, Ekaterinburg, Russia; N. Zhuravlev, E. Zabolotskaya, Inst. of Solid State Chem., Urals Div. RAS, Ekaterinburg, Russia

Compounds with the olivine-type structures are considered as perspective materials for lithium-ion power sources for both industrial and transport applications. Lithium iron phosphate is most highly developed from this family, but LiMnPO4 is supposed as much promising, due to its higher EMF vs. lithium. One of the main lacks of this class of materials is the low electronic conductivity. The traditional ways of conductivity increase by doping with transition metal for both LiFePO4, and LiMnPO4 do not result to essential success, or limit specific capacity. Our approach consisting in the influence onto anion sublattice of substance results to the best effect. In contrast with initial substance, such solid solutions are suitable for oxygen nonstoichiometry creation. The optimal synthesis conditions as well as homogeneity limits of LiMnP1-xVxO4-delta solid solutions were determined. Positions of vanadium together with the valence state for both manganese and vanadium ions were studied by a variety of methods (NMR, ESR, magnetic susceptibility). It was shown, that doping of LiMnPO4 with vanadium jointly with oxygen nonstoichiometry presence brings to substantial enhance of electronic conductivity in this material.

CF:P14 **Direct Synthesis of Lithium Ion Electrode Composition**

V. Gorshkov*, B. Tsarev, OOO Eliont, Ekaterinburg, Russia; D. Kellerman, Inst. of Solid State Chem., Urals Div. RAS, Ekaterinburg, Russia

The electrode materials for lithium-ion power sources should possess good electronic conductivity for maintenance of high working currents. This requirement is provided traditionally by carbon immission into an active material. "In situ" methods of electrode compositions synthesis were reasonable step in development of this approach. We have developed a method of reception of a composite consisting of electrochemically active matrix, for example Li4Ti5O12, LiMePO4, or LiMeSiO4 (where Me - Fe or Mn) and surface carbon film, up to graphene-like monolayer. Such approach allows to minimize the weight share of conductive additive, and to combine the stages of both synthesis of the material and the creation of the composition. This technique consists in the synthesis of oxide material in controlled gas atmosphere with an active reductive gas. During the synthesis, a condensation of carbon in its various forms takes place. The conditions for the formation of the graphene layers, as well as the influence of these layers on dispersity of the material, are discussed. Detailed results for lithium titanate and applicability of the method to other materials are shown.

CF:P17 **Production of Nano Size TiO2 Sol and Highly Efficient Photocatalytic TiO2 Powder by Mechanical Ball Milling**

E. Corapci[1]*, B. Aysin[1], J. Park[2], A. Ozturk[1], [1]Dept. of Metallugical and Materials Engineering, Middle East Technical University, Ankara, Turkey; [2]Dept. of Materials Engineering, Atilim University, Ankara, Turkey

Titanium dioxide (TiO2) is most widely studied as a photocatalytic material as compared to the others since it has higher photocatalytic activity. In this respect, this study was carried out to produce simultaneously nano-size TiO2 sol and high-efficient photocatalytic TiO2 powder by mechanical milling. Starting material was crystallized photocatalyst TiO2 which had average particle size of 1 µm and crystalline phase consisted >95% anatase. Milling was carried out by using zirconia balls with 1 mm diameter in a 1 lt capacity zirconia jar. After milling operation, the nano and micron size particles were separated with centrifugal separator. Particle size analyzer was used to determine particle size and size distribution. Then, XRD, EDS and SEM analysis were carried out in order to investigate the changes in microstructure, phases and composition after mechanical milling. Finally, in order to determine photocatalytic activity of micron size powder and nano size sol, gas - bag, methylene blue, outdoor and wettability tests were carried out. Results revealed that, photocatalytic activity of TiO2 increased as the particle size decreased.

CF:P19 **Photocatalytic Redox Reaction of Nitro Aromatics and Secondly Alcohols to Amino Aromatics and Ketones in Suspension of Titanium(IV) Oxide**

Kazuya Imamura*, Shin-ichi Iwasaki, Tsuyoshi Maeda, Keiji Hashimoto, Hiroshi Kominami, Kinki University, Higashi-Osaka, Japan

Aromatic amines are important compounds because they are intermediates of medicines and dye compounds. There have been many papers on reduction of nitro compounds to amines by photocatalysis of titanium(IV) oxide. In most cases, alcohols were used as both solvent and hole scavenger. Alcohol scavengers are generally oxidized to poisonous aldehyde with hole. We have already reported that photocatalytic reduction of nitrobenzene (NB) selectively gave aniline (AN) in aqueous suspensions of TiO2 in the presence of oxalic acid (OA) as hole scavenger. The scavenger was converted to untoxic carbon dioxide (CO2) in photocatalytic reduction of NB. This photocatalytic reduction of NB is greener process than the reduction using methanol.

However, hole scavenger is only decomposed to CO2 with hole. In this study, we found that m-nitrobenzenesulfonic acid (m-NBS) was photocatalytically reduced to m-aminobenzenesulfonic acid (m-ABS) in 2-propanol (2-Pro) suspension of TiO2 and that 2-Pro was oxidized to acetone with a high stoichiometry.

CF:P20 **Degradation of Organic Acids in Aqueous Suspensions of Gold/Cerium(IV) Oxide Powder Under Irradiation of Visible Light**

A. Tanaka*, K. Hashimoto, H. Kominami, Kinki University, Higashi-Osaka, Japan

Gold (Au) nanoparticles supported on cerium(IV) oxide powder showed strong absorption at around 550 nm due to localized surface plasmon resonance(LSPR) of Au and exhibited a higher level of activity than other Au-supporting samples (Au/TiO2, Au/ZrO2, Au/SiO2) did in mineralization of organic acids in aqueous suspensions under irradiation of visible light (> ca. 520 nm).

CF:P21 **Correlation Between Physical Properties and Photo-catalytic Activities of Metal Ion-titanium Oxide Responding to Visible Light**

S. Kitano*, K. Hashimoto, Kinki University, Higashi-Osaka, Japan

It is known that titanium(IV) oxide (TiO2) works as a semiconductor photocatalyst that is able to decompose harmful organic compounds. Since TiO2 only absorbs UV light, TiO2 does not exhibit photocatalytic activity under irradiation of visible light. Therefore, development of a photocatalyst responding to visible light is very important for effective utilization of solar energy. Recently, it was reported that rutile type-TiO2 modified with Cu2+ exhibited good photocatalytic activity for decomposition of volatile organic compounds (VOC) under irradiation of visible light. We have reported that TiO2 modified with RhCl3 showed excellent photocatalytic activity for oxidative removal of NOx under irradiation of visible light. In this study, TiO2 samples having various physical properties were prepared using solvothermal method and modified with Cu2+ or Rh3+. Then, correlation between physical properties and photocatalytic activities in degradation of VOC under irradiation of visible light was investigated.

CF:P22 **Preparation and Characterization of Complex Oxides for Water Photolysis**

Eui-Chol Shin*, Yong Kim, Hyun-Ho Seo, Jong-Sook Lee, Chonnam National University, Gwangju, Korea

We prepared and characterized several oxides in tunnel and layered structure based on the MO6 octahedra (M=Ti,Nb) with alkali and alkaline earth metals (Na, K, Ba, La) as interstitials, known for high catalytic activity for water photolysis. The nominal compositions by the solid state reactions prepared were K2Ti3O7, K2Ti4O9, K2Ti6O13, Na2Ti3O7, Na2Ti4O9, K2Ti6O13, La2Ti2O5, K4Nb6O17 and K2La2Ti3O10. The crystal structure and phase compositions were examined by the X-ray diffraction and compared with the previously reported phase diagrams. Especially, Na2O-TiO2 and K2O-TiO2 systems were systematically compared. Microstructural investigation revealed the formation of needle- and plate-shape grains in many compositions representing the characteristic crystallographic anisotropy. Impedance spectroscopy has been applied to investigate the dielectric and conductive behavior of the compositions in relation with crystal structure and microstructures.

CF:P23 **Sintering by Activated Surface of Cermet Materials**

T.G. Restivo*, C. Yamagata, S.R.H. Mello-Castanho, Nuclear and Energetic Research Institute - IPEN, Sao Paulo, SP, Brazil

Cermet materials have become of great importance once they can combine and improve both metal and ceramic properties, including functional ones. Electrodes based on YSZ-Ni are the key components for solid oxide fuel cells (SOFC) and high temperature electrolysis (HTE) devices. The direct preparation of such cermets from metallic and ceramic constituents is desired in order to reduce the processing steps. However, sintering process often fails to attain the suitable density and porosity for the applications. The work proposes a new process route that makes use of a particular cermet powder morphology - pod-like - which displays higher sinterability by means of the integrated sintering by activated surface (SAS) mode. The concept involves the ceramic particles plating by thin metallic films at a nanometric level, therefore blocking the earlier surface diffusion, conserving the powder activity. Two powders preparation methods are investigated: mechanical alloying and electroless metal plating. Some metallic additives are admixed to trigger the SAS effect like copper, refractory metals and silver. The SAS process is carried out under controlled oxygen potential to drive the desired surface reactions. The process results of doped YSZ-Ni have demonstrated the sintering temperature can be anticipated by 300 °C for the same densification while the controlled partial oxygen pressure has shown a large influence on the final density and microstructure. Ceramic bodies containing 5-10 vol.% metals can be also consolidated up to the closing point of the inner porosity, being suitable to structural applications. Cermet powders and sintered pellets in different conditions are studied and characterized by X-ray diffraction and electron microscopy. The quasi-isothermal sintering kinetics method is employed as a tool to confirm the activated sintering. Electrical conductance and redox behavior are evaluated for the cermet materials to assure a good performance as SOFC and THE electrode.

Symposium CG

CERAMIC THIN FILMS AND COATINGS FOR PROTECTIVE TRIBOLOGICAL AND MULTIFUNCTIONAL APPLICATIONS

Oral Presentations

Session CG-1

Advances in Deposition, Surface Modification and Characterisation

CG-1:IL01 **Recent Developments in Thermal Spray Processes**

P. Fauchais, SPCTS, UMR 6638, University of Limoges, Limoges, France

During the last decade thermal spray processes have made great strides: - New powder production techniques: cryomilling (nanometer sized ceramic particles or mechanical alloying with nano sized grains), new iron complex alloy particles producing amorphous coatings, micrometer-sized agglomerated nanometer-sized particles; - A better understanding of cold spray process with interesting developments in cermet coatings; - New HVOF guns with high velocity (>500m/s) and low temperature (close or below melting) particles; - Sensors, able to work in the harsh environment of spray booths, measuring hot or cold particle characteristics in flight ... that have drastically improved coatings reproducibility and reliability; - Nano structure coatings with: i. spraying only partially melted micrometer-sized agglomerated nanometer-sized particles, ii. spraying suspensions of nanometer-sized particles or solutions of particles precursors. Nanostructure coatings are produced with porosities in the nanometers range and thickness between 5 µm and a few hundreds µm. However new problems have shown up such as the liquid injection, its interaction with hot gases, heat and momentum transfers to nanometer-sized particles, effects of very high heat fluxes (up to 20-30 MW/m2).

CG-1:IL02 **New Horizons for Ceramic Coatings and Films Produced by Plasma Electrolytic Processes**

A. Yerokhin*, A. Matthews, Dept. of Engineering Materials, University of Sheffield, Sheffield, UK

An overview is given to the research progress in advanced Plasma Electrolytic Oxidation (PEO) processes for coating lightweight metals, e.g. Al, Mg and Ti. Originally developed to enhance barrier protection performance of anodic oxide films, whilst providing ecologically friendly alternatives to conventional anodising methods, PEO relays on modifying effects of microdischarge phenomena that accompany coating formation. Superior protective properties of PEO coatings are associated with macroscopically dense ceramic-like structures formed due to local high-rate heating and quenching of the coating material at the microdischarge sites. Relevant research is focused on discharge understanding and control through application of AC and pulsed current modes. Incorporation of electrolyte species into the coating structure constitutes another distinctive feature of PEO. Appropriate modification of electrolyte composition enables in-situ formation of complex oxide-based compounds on the metal surface. This is utilised in development of PEO coatings with enhanced functional properties, including biological and catalytic activity. Examples are given to the characteristics, properties and applications of functional PEO coatings as well as associated hybrid and duplex coating systems.

CG-1:IL03 **Recent Achievements in Laser Cladding Technologies**

Petri Vuoristo, Tampere University of Technology, Department of Materials Science Surface Engineering, Tampere, Finland

Recent developments in laser cladding technologies are reviewed in the presentation. Laser cladding (laser coating) with its latest developments steps is a novel coating process, which produces coatings with high density, metallurgical bonding, and low total heat input to the substrate. Modern laser power sources, laser cladding processes including hybrid processes, coating materials and properties are reviewed with practical examples. Such properties as corrosion resistance and wear properties are presented and compared with coatings produced by other deposition methods, e.g. thermal spraying, galvanic processes, weld surfacing etc. Typical application areas of laser coatings are described. Latest developments in laser cladding activities in Finland are presented. Examples of R&D collaboration between a university, a regional technology centre, and an industrial laser cladding company is described.

CG-1:L05 **Cold Spray Deposition of TiO2 Nanostructured Particles**

Motohiro Yamada[1]*, Hiroaki Isago[2], Koichiro Shima[2], Hiromi Nakano[1], Masahiro Fukumoto[1], [1]Toyohashi University of Technology; [2]Graduate student, Toyohashi University of Technology, Toyohashi, Japan

Cold spray process has been developed as the coating technology for soft metals. In this process, solid particles accelerated by ultrasonic gas flow and deposit onto the substrate surface and adhere with plastic deformation. Therefore, it was considered to be difficult to fabricate ceramic coatings. In this study, TiO2 coatings were fabricated by cold spray process and the deposition behavior of sprayed particles were investigated. It was possible to fabricate TiO2 ceramic coatings by cold spray process. The deposition efficiency was increased with both working gas temperature and pressure. It means that the increasing of gas velocity increase the particle velocity and the deposition efficiency. Therefore, it is considered that the sprayed TiO2 ceramic particles deposit with deformation like metallic particles on the substrate by the kinetic energy. TEM observation of the feedstock particle exhibited that the particle consists of nano-scaled fine primary particles. This structure of particle achieved fabrication of TiO2 ceramic coating by cold spray process.

CG-1:IL06 **A New High Speed and Low Temperature Coating by Laser Chemical Vapor Deposition**

T. Goto, Institute for Materials Research, Tohoku University, Sendai, Japan

Chemical vapor deposition (CVD) has been generally understood as a thin-film and high-temperature process. If CVD can be applied onto non-refractory substrates, CVD can be more widely applied. Auxiliary energy such as plasma and light can accelerate CVD enabling low temperature deposition; however those CVDs have been scarcely employed to thick coatings. We have developed a new laser CVD for thick coatings at relatively low temperatures using a high power laser (250 W). A plasma formation around substrate might be a main reason of the high-speed and low-temperature deposition. We have synthesized many films including ZrO2, Y2O3, TiO2, Hydroxyapatite, SiC, TiN. This paper mainly focuses on the preparation of α-Al2O3 film as a top-coat for cutting tools. α-Al2O3 film was obtained at around 800 K which was 400 K lower than that of conventional CVD. The cross-section shows a columnar feather-like texture containing a large amount of nano-sized pores, advantageous for thermal insulation for cutting tools. Highly (006), (104) and (012) oriented α-Al2O3 films with well-developed hexagonal grains were obtained. The highest deposition rate of α-Al2O3 film was about 350 µm/h, which was more than 100 times greater than those of conventional CVD.

CG-1:IL07 **3-D Static and Time-depending Modeling of RF and DC Thermal Plasmas for Industrial Applications**

V. Colombo*, E. Ghedini, P. Sanibondi, Dept. of Mechanical Engineering, University of Bologna, Bologna, Italy

Thermal plasma processes play nowadays a key role in many industrial applications, such as powder densification and spheroidization, synthesis of nano-powders, treatment of waste materials and spraying of thin coatings. Although many of these applications have been fully implemented industrially for many decades, modeling plays an important factor in their continued development and improvement. 3-D simulation of the behavior of commercial inductively coupled (RF) plasma torches with non-axisymmetric reaction chamber can be useful tool to predict the main features of plasma assisted treating and processing of injected raw materials. The effects of changing coil current frequency, the hydrogen mixing in an argon primary gas and the flow patterns and temperature distributions have been investigated. 3-D time-dependent modeling DC non-transferred arc plasma torch for plasma spraying operating at atmospheric pressure can allow the prediction of particle trajectories and thermal history, the analysis of the influence of the plasma jet cold gas entrained eddies on particle behavior and the mechanisms that can lead to a fluctuating and non homogeneous heating of the particle stream. All computations have been performed using a customized version of the CFD commercial code FLUENT©.

CG-1:L08 **Fabrication, Structural and Mechanical Properties of Aluminium Oxide Thick Films Using Aerosol Deposition**

S. Hirose*, Y. Ezuka, N. Sakamoto, S. Oh, J-H. Park, J. Akedo, AIST, Tsukuba, Japan

The thick Aluminum oxide is seems to be a great important material due to high hardness, high wear resistance, chemically stable in both acid and alkali environments, good biocompatibility, and etc. Aerosol deposition (AD) is seems to be usuful for obtaining thick film because high quality aluminum Oxide ceramic film can be formed directly on any substrate material without pretreatment of substrate. In this presentation, we show the stractual and mechanical properties formed by AD method. a-phase Al2O3 film were prepared on stainless steel at room temperature when usinga-phase Al2O3 powder as a starting material. The hardness of Al2O3 coating film was dramatically changed from 700 to 1500HV with increasing pre-heating temperature of Al2O3 powder. The highest value of hardness of Al2O3 coating film was close to that of Al2O3 bulk material. Also, friction coefficient and wear rate of Al2O3 coating (2.5 µm) were also achieved as those of Al2O3 bulk material. And, the wear rate of Al2O3 coating (2.5 µm) was decreased 200 times lower than that of substrate. These results show the possibility for applying AD method for the future practical use in the mechanical engineering field.

CG-1:L09 **A Comparison Between Conventional Thermal Treatment and Excimer Laser Irradiation Performed on Alumina/PEEK Composite Coatings**

M.F. De Riccardis*, V. Martina, D. Carbone, R. Terzi, ENEA, Brindisi Reseach Centre, Brindisi, Italy; A.P. Caricato, G. Leggieri, Dipartimento di Fisica, Università del Salento, Lecce, Italy

High performance polymer composites reinforced with ceramic particles result in a unique combination of properties, which make them useful in aerospace, microelectronic, automotive, and biomedical applications. By introducing fillers in polymers, composite properties can be appropriately tailored. Amongst inorganic fillers, alumina have been one of the most used for its oxidation and wear resistance. The inclusion of alumina particles in a high performance polymer such as poly(etherether-ketone) (PEEK) is particularly interesting when one wants to obtain a higher thermal and mechanical performances polymer. Optimised alcoholic suspensions containing Alumina particles and PEEK powder were used to deposit composite functional coatings on conducting substrates by Electrophoretic Deposition (EPD). To reduce the intrinsic porosity of EPD composite coatings, conventional thermal treatments were conducted in a furnace at the melting temperature of PEEK. In order to compare, non-conventional thermal treatments were performed by pulsed KrF laser irradiation (248 nm). The effects of the different treatments, one in stationary and the other in transient condition, on the morphological, structural and microanalytical properties of the coatings were studied.

CG-1:IL10 **Mechanical Properties of Composite Films Consisting of Silicon Nanopillars Embedded in a Nanostructured SiC Matrix**

A.R. Beaber[1], W.W. Gerberich[1], S.L. Girshick[2]*, [1]Dept. of Chemical Eng. and Materials Science, University of Minnesota, Minneapolis, MN, USA; [2]Dept. of Mechanical Engineering, University of Minnesota, Minneapolis, MN, USA

Coatings with high wear-resistance have generated a great deal of interest due to a diverse range of applications, including cutting tools, turbine blades, and biomedical joint replacements. Ceramic nanocomposites offer a potential combination of high strength and toughness that is ideal for such environments. In the current study, Si-SiC nanocomposites were deposited using a hybrid of chemical vapor deposition and nanoparticle ballistic impaction. A nanocrystalline (nc) 3C-SiC matrix was grown on (111) Si substrates by impacting SiC nanoparticles and simultaneously exposing the substrate to an environment saturated with carbon and silicon vapors. In addition, the substrate was seeded with an ordered array of Au nanoparticles, which act as 2D nucleation and growth sites for (111) Si nanopillars via vapor-liquid-solid growth. Together, these growth mechanisms create a nanocomposite film composed of Si nanopillars surrounded by a nc-SiC matrix. Nanoindentation and micro-Raman spectroscopy were used to measure the residual stresses in the matrix and nanopillars. Increases in yield strength and fracture toughness are explained through a combination of length scale effects and localized thermal mismatch stresses induced at the Si-SiC interfaces.

CG-1:L12 Suspension Plasma Spraying - Influence of Spraying Parameters on Yttria Stabilized Zirconia Coatings Microstructure

K. Wittmann-Teneze*, J. Toulc'hoat, E. Bruneton, E. Estrade, CEA DAM Le Ripault, Monts, France

Suspension plasma spraying (SPS) offers the possibility to manufacture thin and fine structured coatings contrary to conventional plasma spraying which is limited to a minimum thickness of about 10 µm. SPS consists in introducing the material to be sprayed as a suspension of micro- or nano-sized particles in a D.C. plasma jet, generated, in this study, by a Sulzer Metco F4VB gun. The present work is a contribution to the understanding of the influence of SPS parameters on yttria stabilized zirconia (YSZ) coatings microstructure and tightness. YSZ was chosen because this material is used at present in two widely studied applications: in the thermal barriers coatings field and as a tight electrolyte in solid oxide fuel cells. With the CEA experimental set-up, some parameters were found to have a strong influence on the coatings characteristics. The most important ones are the spraying atmosphere, the substrate temperature, the suspension solvent, the gas diffuser inside the plasma torch and the standoff distance. A less important role was demonstrated for other parameters such as the diameter of the suspension injector or the injection pressure.

CG-1:L13 Characterization of Thin Films in Silicate Surfaces

L. Fröberg*, M. Piispanen, L. Hupa, Process Chemistry Centre, Åbo Akademi University, Turku, Finland

Composition of surface layers controls the properties of silicate surfaces in several applications. On bioactive glasses the double layer consisting of an inner silica layer and outer hydroxyapatite layer is essential for bonding of the glass with bone. When developing glazes or functional coatings for glazes, an understanding of interfacial reactions between the different layers is important. In this work we discuss the use of different surface characterization methods for measuring the composition and thickness of thin layers on silicate surfaces. Surface composition was characterized by SEM-EDX and XPS. Surface topography was established by white-light confocal microscopy and AFM. Layer thicknesses and composition gradients were measured from cross-sections using SEM-EDX and by XPS depth profiling. XPS gave valuable information about elemental gradients through the surface layers. Film thickness measurement was laborious by XPS due to insulating properties of glass, but the results were comparable to cross-section analysis by SEM-EDX. Effort was put in preparation of representative samples of each surface and sample type, e.g. plates and fibers. The parameters and suitability of the instrumental methods for characterization of silicate surfaces will be discussed in detail.

CG-1:IL14 Development of Methodology of Fracture Toughness for Thin Films and Coatings

Sam Zhang*, Xiaomin Zhang, School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore

Unlike bulk materials, fracture toughness of thin films and coatings is not well defined nor the measurement standardized. Though many methods are in use today, such as nano-indentation, scratch adhesion, three-point or four-point bending, two-step tension, etc. they are at most estimation, not measuring the fracture toughness in its true sense. Some are even confusing or contradicting to each other. This talk focuses on development of the methodology of fracture toughness for thin films and coatings starting with clarification of toughness and fracture toughness, fracture toughness of freestanding films and that of coatings, and deals with issues related to stable and unstable cracking during measurement. This talk will also cover the newest development in the field where a coating is deposited on a pre-cracked wafer that is then forced open to induce crack propagation in the coating. The strain measured during fracture of the film is used to calculate the fracture toughness. A case study using DLC film will be presented.

CG-1:IL15 Possibilities in Characterization of Ceramic Thin Coatings Pore Microstructures by Synchrotron X-ray Imaging and Scattering Techniques

Jan Ilavsky, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA

Complexity, wide size ranges, and often anisotropy are attributes that can describe porous microstructures of ceramic thin coatings, such as those deposited by thermal spray techniques. This microstructure complexity presents especially difficult challenges for routine characterization, since a number of commonly applied methods have significant limitations. Recently developed synchrotron-based X-ray techniques can provide significant help in this area. This talk will discuss the main principals, advantages, and disadvantages of X-ray imaging and scattering techniques employing synchrotron radiation. It will be shown that, while no technique in itself is sufficient for these challenging materials, in combination it is possible to have a sufficiently complex characterization protocol available. A realistic but capable characterization protocol may need to combine "in-house" tools complemented by targeted application of presented scattering and imaging techniques. Examples of successful application to EB-PVD and suspension plasma-sprayed ceramic coatings will be shown.

** Work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357*

CG-1:L16 Characteristics of $BaTiO_3/LaNiO_3$ and $Ba_{0.48}Sr_{0.52}TiO_3/LaNiO_3$ Artificial Superlattices Films Prepared by RF Magnetron Sputtering

Hsin-Yi Lee, National Synchrotron Radiation Research Center, Hsinchu, Taiwan

We have successfully fabricated high quality of $BaTiO_3/LaNiO_3$ (BTO/LNO) and $(Ba_{0.48}Sr_{0.52})TiO_3/LaNiO_3$ (BST/LNO) superlattices on an Nb-doped $SrTiO_3$ (STO) substrate by rf magnetron sputtering. X-ray reflectivity and high-resolution diffraction measurements were employed to characterize the microstructure of these films. The formation of a superlattice structure was confirmed through both the appearance of Bragg peaks separated by Kiessig fringes in x-ray reflectivity curves and the satellite peaks of a (002) diffraction pattern and the secondary-ion mass spectrometry (SIMS) profile. The appearance of discernible satellite peaks beside the main peak of the crystal truncation rod observed for deposited films clearly demonstrates that a well defined superlattices structure is achievable through rf sputtering growth. These BTO/LNO or BST/LNO superlattices films reveal a partial strain relaxation and not fully strained state for all modulation length even though the thickness of individual BTO or BST and LNO layers is less than the critical thickness. The dielectric properties of BTO/LNO and BST/LNO superlattices show a significant enhancement with respect to the BTO or BST single layer with the same thickness. From a macroscopic point of view, the strain in the superlattice structure contributes significantly to the dielectric enhancement.

CG-1:L17 The Role of Multi-layering in Controlling Contact Damage in Nitride Based Hard Coatings: TiAlN-TiN and ZrN-Zr

N. Verma, S. Math, V. Jayaram*, S.K. Biswas, Indian Institute of Science, Bangalore, India

In the present work, we describe, using indentation, focused ion beam machining and transmission electron microscopy, the evolution of damage in 2 model systems, i.e., TiAlN-TiN and ZrN-Zr. The former is an isostructural combination while the latter is a metal-nitride combination that does not display sub-nitrides. In the case of TiN-AlTiN, it is shown that flaw nucleation, that stems from column boundary sliding does not lead to large scale propagation, while column sliding itself is replaced by a more homogeneous deformation near the upper portion of the film. Both these features increase with multilayer density, thus pointing to a role of interfaces in reducing the stress concentration that arises during columnar shear. In the case of ZrN-Zr, while the soft phase interrupts cracking in the nitride, too thick a metal layer can also act to initiate flaws in the nitride. This stress-raising action of a soft layer, which is expected at the film-substrate interface, may also be predicted within a multilayer from elastic calculations of the stress field around spherical contacts using the well known integral transform solutions. Thus, these results point to the possible existence of an ideal metal-nitride proportion to maximize the toughening role of a ductile interlayer.

CG-1:L18 Ti-Si-C Films Formed by Dual Beam Ion Assisted Deposition

Agnieszka Twardowska[1]*, Boguslaw Rajchel[2], Lucyna Jaworska[1, 3], [1]Institute of Technology, Pedagogical University, Krakow, Poland; [2]Institute of Nuclear Physics, Polish Academy of Sciences, Krakow, Poland; [3]Institute of Advanced Manufacturing Technology, Krakow, Poland

Ti-Si-C coatings were formed at room temperature on AISI 316L steel substrates by dual beam ion assisted deposition technique from single compound Ti_3SiC_2 target. Scanning and transmission electron microcopy method were used to examine as-deposited coatings. Their morphology was smooth and dense and their thickness were in the range 100 nm to 1µm. Raman spectra of coated substrates were collected with five peaks at the same positions as for Ti_3SiC_2 compound target. TEM and HRTEM examinations, accompanied by SAED analyses revealed that deposited films were amorphous. Nanoindentation tests were provided on coated and uncoated substrates and hardness H_{IT} and reduced elastic modulus E_{IT} were calculated using the Oliver & Pharr method.

Session CG-2

High Performance Protective Coatings in Oxidizing and Harsh Environments

---

CG-2:IL01 Design of Super- (H>40 GPa) and Ultrahard (H>80 GPa) Nanocomposite Coatings: Theoretical Background, Experiments, and Industrial Applications

Stan Veprek, Department of Chemistry, Technical University Munich, Garching, Germany

Intrinsically super- and ultrahard materials attain high hardness from their large intrinsic strength, whereas extrinsically super- and ultrahard materials reach such hardness due to their nanostructure. The recent search for intrinsically super- and ultrahard materials concentrates on those with high elastic moduli. I shall show several examples of materials with high zero-pressure elastic moduli but relatively low hardness, because, upon large imposed shear strain, where plastic deformation occurs on the atomic level, they undergo an instability of the electronic structure. Such softening does not occur in the super- and ultrahard nc-TmN/a-Si3N4 nanocomposites (TmN = hard transition metal nitride), in which 3-4 nm size TmN nanocrystals are “glued” together by about 1 monolayer thick SiNx interface. A combined ab initio DFT calculation of the shear strength of the interface, Sachs averaging of the shear resistance of the interfaces of randomly oriented nanocrystals, pressure enhancement of the flow stress and Tabor’s relation between the hardness H and yield strength Y shows that these materials can reach hardness significantly larger than diamond, when correctly prepared and essentially free of defects, as we have earlier shown experimentally.

CG-2:IL02 Environmental Barrier Coatings for Ceramic Matrix Composites

Kang N Lee, Rolls Royce Corporation, Indianapolis, IN, USA

Ceramic matrix composites (CMC) offer structural materials solutions to increasing the efficiency and performance of next generation gas turbine engines due to their high temperature capabilities and low densities. One key drawback of silicon-based CMCs is the recession of SiC due to the volatilization of silica scale by high temperature, high velocity water vapor. External environmental barrier coatings (EBC) have been developed to protect CMCs from water vapor attack. The 1st generation EBC was developed in NASA’s HSCT-EPM Program in mid 1990’s, which was later applied on combustor liners of a Solar Turbines’ industrial gas turbine engine, enabling the world’s first successful field test of SiC/SiC combustor liners in gas turbine engines in late 1990’s. Significant progress has been made on EBCs since that time through intensive R&D efforts in government labs and OEMs. This paper will review the evolution of EBCs and the current status.

CG-2:L04 Nanolaminated Coatings in the Y2O3-Al2O3-ZrO2 System Deposited by MOCVD

N.K. Eils*, P. Mechnich, DLR, Institute of Materials Research, Cologne, Germany; H. Keune, Technical University of Braunschweig, Institute of Surface Technology, Germany

Oxide ceramic coatings in the Y2O3-Al2O3-ZrO2 system were deposited by metal-organic chemical vapor deposition (MOCVD) using a screw feeding system with flash evaporation. Therefore the gas phase composition should be homogenous. Nevertheless the coatings show a nanolamellar microstructure due to through thickness small-scaled stoichiometry fluctuations. Several experiments were carried out with modified composition of the starting material. The Y/Al molar ratio was set to 1/1 for all precursor mixtures while the content of zirconium in the mixture was systematically varied to achieve ZrO2 contents in the range from 0 to 50 mol % in the coatings. Annealing experiments in air and flowing water vapor at temperatures up to 1200°C were carried out to study the microstructural development. XRD was used to analyze phase transformations while the coating microstructure was investigated in detail by means of SEM. After heat treatment the lamellar character of the coatings maintains although phase transformation occurs. In this state the lamellae result from phase separation and linear porosity. Coatings which include a significant content of ZrO2 show alternating sequences of nanometer-sized YSZ and yttrium aluminates.

CG-2:L05 Precursor-derived, Ultra-thin Aluminophosphate Protective Coatings

Benjamin Mangrich*, Sankar Sambasivan, Applied Thin Films, Inc., Evanston, IL, USA

Recent advances in the development of ceramic coatings for protection against harsh environments continue to push the boundaries of material performance. Many of these coatings however, require complicated and expensive deposition techniques, or are limited in applicability due to thermal incompatibility with substrates at elevated temperatures. A novel precursor derived aluminophosphate coating has been developed with thickness below 1 micron. Sluggish diffusivity within the material enables high temperature stability of the amorphous structure and barrier properties up to 1400 °C The coating has been shown to protect a variety of metallic and ceramic materials against oxidation and corrosion at high temperatures, extending lifetime and usefulness.

CG-2:L06 Particle-filled Polysilazane-based Coatings on Steel

M. Günthner*, T. Kraus, W. Krenkel, G. Motz, University of Bayreuth, Ceramic Materials Engineering (CME), Bayreuth, Germany; D. Decker, Clariant Advanced Materials GmbH, Sulzbach am Taunus, Germany

Precursor-based composite coatings were developed as protective coatings on steel against oxidation and corrosion using a preceramic polymer in the system SiN and BN particles as a passive filler. After stabilising the optimised coating suspension by stirring and ultrasonic agitation, coatings were applied on different steel substrates by the dip-coating technique. The excellent adhesion of the filled coatings results from the formation of direct chemical bonds between the coating and the steel. After thermal treatment in air at temperatures up to 800 °C, microstructural analysis reveal the formation of a composite coating of BN particles in an amorphous ceramic SiNO matrix. Uniform, dense and crack-free coatings with a thickness of about 12 µm were achieved. The composite coatings exhibit significant potential for protecting mild steel against oxidation up to 700 °C. Parabolic oxidation kinetics and a reduced weight gain up to two orders in magnitude were determined. Furthermore, the complete handling and pyrolysis of the precursor coatings can be applied in air leading to a more effective and low-cost process. This makes them interesting as high temperature protective coatings, e.g. for exhaust systems, waste incineration plants or for applications in the chemical industry.

CG-2:IL07 Durability of Materials at High Temperature

J.L. Grosseau-Poussard, Laboratoire d’Etudes des Matériaux en Milieux Agressifs (LEMMA), EA-3167, FREDD-CNRS, Université de La Rochelle, Pôle Sciences et Technologie, Bâtiment Marie Curie, La Rochelle cedex, France

Materials are subjected to high temperature corrosion/oxidation in numerous technical processes and environments. The most obvious are turbines, engines and power stations. The lifetime of the components strongly depends on both the chemical and mechanical integrity of the oxide/metal system. Moreover, protective coatings or surface treatments aimed at improving the high-temperature thermal, chemical and physical degradation of materials in both oxidising and harsh environments are often employed. Consequently, the degradation processes and life-time have to be evaluated. In the present work, different examples of metallic materials used in high temperature processes will be considered to illustrate how the durability and the failure mechanisms can be determined. When additional surface treatment is applied, the way it modifies the oxidation mechanisms will be review with the consequence on the ageing phenomena.

CG-2:L08 Mechanical and Surface Properties of Chemical Vapor Deposited Protective Aluminum Oxide Films on TA6V Alloy

D. Samélor, M. Aufray, N. Pébère, C. Vahlas*, Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux, Toulouse, France; Y. Balcaen, J. Alexis, L. Lacroix, J-D. Beguin, Université de Toulouse, INP/ENIT, LGP, Tarbes, France

Mechanical and surface properties of aluminum oxide films were investigated by nanoindentation, microscratch and micro tensile tests, by contact angle measurement and electrochemical impedance. The films were grown on TA6V substrates by a low pressure MOCVD process from aluminium tri-isopropoxide. Films grown at 350 °C are amorphous AlO(OH), the one at 480 °C are amorphous Al_2O_3 and the one at 700 °C are nanocrystalline g- Al_2O_3. Scratch tests and micro tensile tests cause adhesive failures on the two films grown at low temperature whereas cohesive failure is observed for the high temperature growth. Similar micro-tensile tests made after corrosion of the specimen with NaCl during 100 h at 450 °C show the beneficial impact of coatings against high temperature corrosion. Contact angle changes approximately from 100 to 50 degrees for films processed at 350-480 °C and 700 °C, respectively. Concerning the electrochemical behavior in salt environment, polarization and electrochemical impedance curves seems to reveal that amorphous alumina coatings improve the corrosion resistance with regard to the bare alloy. These consolidated results reveal promising combination of properties for the films grown at different temperatures with regard to the targeted applications.

CG-2:L09 Oxidation Behavior of Thermal Barrier Coatings on Copper Substrates

Jana Schloesser*, Joachim Rösler, Martin Bäker, Technische Universität Braunschweig, Institut für Werkstoffe, Braunschweig, Germany

In rocket engine combustion chambers the cooling channels experience extremely high temperatures and environmental attack. Thermal protection can be provided by Thermal Barrier Coatings. Because of the good heat conduction the inner combustion liner is made of copper. The performance of a standard coating system for nickel based substrates is investigated on copper substrates. Thermal cycling experiments are performed on the coated samples. Due to temperature limitations of the copper substrate material, no thermally grown oxide at the interface of the thermal barrier coating and the bond coat forms. Delamination of the coatings occurs at the interface between the substrate and the bond coat due to oxide formation of the copper at uncoated edges. In real service a totally dense coating can probably not be assured which is the reason why this failure mode is of importance. Different parameters are used for thermal cycling to understand the underlying mechanisms of delamination. Furthermore, finite element simulations of the thermal cycles are performed to evaluate elastic cooling stresses. The influence of the copper oxide formation on the elastic stress state is investigated.

CG-2:L10 Water Corrosion of Mullite-based EBC Multilayer Coatings

E. Garcia*, J. Mesquita-Guimaraes, P. Miranzo, M.I. Osendi; Instituto de Ceramica y Vidrio (CSIC), Madrid, Spain; C.V. Cojocaru, Y. Wang, C. Moreau, R.S. Lima; National Research Council of Canada, Boucherville, QC, Canada

Mullite and mullite/ZrO2 systems can be considered as environment barrier coatings (EBCs) for protection of Si-based (Si3N4, SiC) substrates against water vapor corrosion for application in forthcoming turbine engines. In this study, single mullite and bi-layer and three-layer coatings of mullite/ZrO2 compositions, engineered to reduce thermal expansion mismatches, were plasma sprayed over Hexoloy SiC substrates. Layers with different characteristics, i.e. porosity and mechanical compliance, were obtained by using different feedstock materials, spray dried and freeze granulated powders. Cracking associated to crystallization issues was controlled through spray coating engineering. The coatings were furnace heat-treated at 1300 °C in a controlled water vapor environment during 100 h. The effect of these corrosion tests was comparatively investigated, putting special emphasis in determining crystalline phases changes by using X- ray diffraction (XRD) and differential thermal analysis (DTA) tools. The microstructures of as-sprayed and exposed coatings were studied by scanning electron microscopy (SEM) and correlated with the results obtained by XRD and DTA analysis. Elastic modulus (E) and hardness (H) of the different coatings were measured by depth indentation methods.

CG-2:IL13 Development of Advanced Coatings for ITER and Future Fusion Devices

Jiri Matejicek*, Pavel Chraska, Institute of Plasma Physics ASCR, Praha, Czech Republic

Thermonuclear fusion is a potential source of cleaner and safer energy for the future. Its technological realization depends on the development of materials able to survive and function in extreme conditions, often involving a variety of loading - thermal, mechanical, chemical and irradiation. This article reviews the development, characteristics and applications of coatings for fusion reactor materials. First, the technological objectives and material-environment interactions are briefly summarized, together with materials requirements and the role of coatings. Then, specific applications in different areas of a fusion device are reviewed, namely the plasma facing components, electrical insulation, diffusion and permeation barriers. Various coating fabrication methods are mentioned and the respective coating characteristics are compared. Selected case studies are presented, with particular focus given to ITER and to ceramic coatings.

CG-2:L14 Overview: How to Quantify the Capability of Yttrium Silicates to be Used as an Environmental Barrier Coating

Francis Rebillat*, Emilie Courcot, University of Bordeaux, Laboratoire des Composites Thermostructuraux (LCTS) UMR 5801, Pessac, France

To be used as environmental barrier coatings, yttrium silicates must be thermally and chemically stable at high temperatures, under high pressures in a moist environment. This work proposes a full method to quantify their thermo chemical and mechanical stabilities: (i) in a corrosive environment at high temperature and (ii) against the covered material to protect. These stabilities were first estimated by thermodynamic calculations and further confirmed with corrosion tests. This first step needed: (i) to measure the partial pressures of yttrium hydroxides through corrosion tests on the simple oxide, Y2O3 and (ii) to extract the free energies of formation of gaseous yttrium-hydroxides formed. In a second step, the measured values of coefficients of thermal expansion (CTE) on these materials allowed identifying what compositions should be preferentially used, to get CTE close to that of the substrate material to prevent delaminating or cracking due to CTE mismatch stress. Finally, these materials are deposited on SiC/SiC composites by plasma spraying. The impact of the morphology, crystallinity, porosity and composition of elaborated coatings on their corrosion behaviour is highlighted.

Session CG-3

Thermal Barrier Coatings

CG-3:IL01 Advanced Thermal Barrier Coatings

Robert Vaßen*, Ophelia Jarligo, Daniel Mack, Tanja Steinke, Detlev Stöver, Institute of Energy Research (IEF-1), Forschungszentrum Jülich GmbH, Germany

Since more than two decades yttria stabilized zirconia (YSZ) has been established as a standard thermal barrier coating material with unique properties as low thermal conductivity, good fracture toughness, high thermal expansion coefficient and excellent processability. However, the efforts to further increase gas turbine efficiencies by increasing inlet temperatures let the YSZ based TBCs reach its limitations in temperature capability. This problem initiated intense efforts to identify new, improved TBC materials. Several interesting classes of materials as pyrochlores, perovskites, (hexa-)aluminates, and also modified zirconia will be presented in this paper. The advantages and disadvantages of the different materials with respect to the needs in a TBC application will be discussed.

CG-3:IL02 Technical and Economical Aspects of Current Thermal Barrier Coating Systems for Gas Turbine Engines

A. Bolcavage, Rolls-Royce Corp., Indianapolis, IN, USA

Advanced thermal barrier coating (TBC) systems for gas turbine engine blade and vane airfoil surfaces consist of electron beam physical vapor deposition (EBPVD) applied yttria-stabilized zirconia plus platinum or Pt-modified diffusion bond coating. Thermally sprayed ceramic and MCrAlY bond coatings, however, are still used extensively for combustors and some turbine section components. This presentation highlights the key features of thermal spray, electroplating, diffusion aluminizing, and EBPVD coating processes. The characteristics of thermally sprayed alloys and ceramics are described. Essential features of a typical EBPVD TBC coating system, consisting of a diffusion bond coating and a columnar TBC, are also presented. The major coating cost elements such as material, equipment, and processing are explained for the different technologies, with a performance and cost comparison given for selected examples.

CG-3:IL03 Thermal Barrier Coatings as an Interacting Multilayer System: Performances and Degradation Mechanisms

O. Lavigne, ONERA-DMSM, Châtillon, France

Thermal barrier coatings are used to protect blades and vanes in the hot sections of gas turbines. These systems consist of a thick porous ceramic layer deposited on an alumina forming metallic bondcoat in contact with the nickel-based superalloy substrate. They are designed to prolong the components lifetimes or to increase gas temperature, and therefore efficiency. In service the structure and composition of the various layers evolve, due to sintering of the ceramic layer, oxidation of the bondcoat, and interdiffusion phenomena with the substrate. As a result the properties of each layer are affected, as well as interfacial toughness. These evolutions, combined with applied external stresses may lead to bondcoat rumpling, crack formation at the bondcoat/ ceramic interface and eventually the ceramic layer may spall off. In addition to these intrinsic degradation modes, interactions with environment can accelerate the system degradation. We will review the rationale sustaining the choice of material constituting each layer, describe their interactions at high temperature and the degradation mechanisms, with illustrations taken from service experience and laboratory tests. Finally we will expose the present challenges to develop more robust and more efficient systems.

CG-3:L04 Thermal Conductivity and Sintering Resistance of Plasma Sprayed Dysprosia-Yttria-Zirconia Thermal Barrier Coatings

Steven Wang, Tom Troczynski*, Dept. of Materials Engineering, The University of British Columbia, Vancouver, BC, Canada; Roger Reed, Dept of Metallurgy and Materials, The University of Birmingham Edgbaston, Birmingham, UK

Yttria-stabilized zirconia has long been the favoured refractory material for demanding applications such as thermal barrier coatings (TBC) on turbine components because of its low thermal conductivity and relatively high thermal expansion coefficient. In recent years however, the demand for higher turbine operating temperatures has led to innovative research in decreasing thermal conductivity and improving sintering resistance of TBC. Rare-earth doped zirconia, rare-earth zirconates, and lanthanum hexa-aluminate have been proposed as candidate materials for the next generation of TBC. This study focuses on dysprosia as a ternary dopant to yttria-stabilized zirconia, examining the relationship of dopant content with overall thermal conductivity and sintering behaviour under cyclic thermal loading between room temperature and 1100 °C. Air plasma spray deposition technique was employed for coatings deposition. This study is prefaced with four hypotheses: 1. increasing levels of dysprosia would likely result in lower overall thermal conductivity; 2. best improvement occurs at about 10 mol% total dopant (Dy + Y); 3. addition of dysprosia is also likely to increase sintering resistance during thermal cycling; 4. higher dopant concentrations, between 10 mol% and 50 mol%, should increasingly lead to shorter coating life under thermal cycling. As-sprayed coating heat capacity, thermal diffusivity, and porosity were measured by differential scanning calorimetry, laser flash method, and image analyses, respectively. Post-cycle coating porosity levels were compared against data for as-sprayed coatings. A theoretical model for estimating the thermal conductivity of plasma sprayed zirconia coatings was derived and constructed from previous works by other researchers. Experimental data and theoretical model presented in this study offer positive confirmations for the above hypotheses, with the exception that increased levels of dysprosia did not result in continued reductions in thermal conductivity.

Session CG-4

Thin Films and Coatings for Tribological and Multifunctional Applications

---

CG-4:IL01 Advanced Ceramic Tribological Layers by Thermal Spray Routes

R. Gadow, University of Stuttgart, Stuttgart, Germany

Protective and functional coatings featuring outstanding tribological performance are of general interest for all kinds of industrial applications i.e for high performance automotive and mechanical applications. Thermal spraying coating technologies play a key role in fabricating hard layers based on ceramic, metal - ceramic and further multiphase materials. Additional functionality can be achieved by combining these coatings with polymer based top coats with low friction coefficient or anti adhesive behaviour. Combined coatings feature also designed thermophysical properties. The presentation will discuss several case studies ranging from automotive applications to paper and printing industry. Thermally sprayed coatings were applied using APS, HVOF and the newly developed HVSFS processes (High Velocity Suspension Spraying) with a special focus on nanoceramic feedstocks. In some applications polymer top coats with dispersed solid phases are applied to enhance functionality. Special aspects in manufacturing engineering are addressed with particular importance not only of the influence of spray process parameters on coating properties but also of spray torch kinematic on hardness, residual stress distribution, dimensional tolerances and porosity distribution will be discussed.

CG-4:IL02 Preparation of TaN-Cu and TaN-Ag Nanocomposite Thin Films and their Anti-wear and Anti-bacteria Behaviors

J.H. Hsieh, Dept. of Materials Engineering, Ming Chi University of Technology, Taishan, Taipei, Taiwan

TaN-metal films were first deposited by reactive co-sputtering on Si and tool steel substrates. The nano-structured films were formed after being annealed using RTA (Rapid Thermal Annealing) at 400 °C for 2, 4, 8 minutes respectively. RTA was used to induce the nucleation and growth of metal particles in TaN matrix and on film surface. AFM, XRD, FESEM, and TEM were applied to characterize the formation of metal nano-particles in and out of the TaN matrix, and to study how they affect the properties of the films. The effects of annealing on anti-wear and anti-bacterial properties of these films were the focus of this study. The results revealed that annealing by RTA could change the properties of these films depending on the formation of metal particles. Consequently, mechanical as well as anti-bacterial behaviors were changed.

CG-4:L03 Low Friction and Wear Resistant Carbon-, MoS2- or Transition Metal Oxide-based Nanocomposite Coatings

B.G. Wendler*, M. Makówka, K. Wlodarczyk, M. Nolbrzak, W.Pawlak, A. Rylski, Lodz University of Technology, Institute of Materials Science and Engineering, Lodz, Poland

A series of low friction and wear resistant carbon-, MoS2- or oxide-based nano-composite coatings have been deposited by means of a non-reactive magne-tron sputtering onto VANADIS 23 HSS steel. The first of the three groups contained a series of nanocomposite coatings of the type nc-MeC/a-C(:H) or nc-MeN/ /a-C(:H) coatings (where Me means Cr or Ti transition metal) in which the the nanocrystallites of the transition metal carbide or nitride were embedded into a hydrogenated or non-hydrogenated amorphous carbon matrix. The second group contained the nanocomposite coatings of the type MoS2(Me) in which the atoms of the same transition metals were embedded into an amorphous MoS2 matrix. The third one contained nanocomposite coatings of the type nc-Ag2O/Me2Ox composed of Ag2O nanocrystallites embedded into an amorphous matrix of Mo or Re or V oxides. A very low wear (~10-16.m3.N-1.m-1) and friction coefficient values from the range (0.04-0.15) during dry sliding at RH 50-54% have been encountered at the condition of a contact pressure <1.5 GPa against a ZrO2 ball 5 mm dia. and for the working temperatures <600 K in case of coatings of the Ist group or <800 K of the IInd one and for the working temperatures from the range 800 K-1100 K for the IIIrd group of the nanocomposite coatings.

CG-4:IL06 Nanocomposite Metal Carbide/Amorphous Carbon Coatings for Tribological Applications

J.C. Sanchez-Lopez*, M.D. Abad, D. Martinez-Martinez, A. Fernandez, Instituto de Ciencia de Materiales de Sevilla (CSIC-Univ. Sevilla), Sevilla, Spain

The design of nanocomposite coatings structures has been the subject of numerous investigations owing to the improvement in hardness, toughness and wear properties. In particular, the combination of nanocrystals of hard ceramic materials as metallic nitrides, borides or carbides in a soft amorphous carbon matrix appears to yield a good compromise between the mechanical and tribological properties. Nevertheless, while many published works report on the correlations between synthesis-structure-properties less is known about the reasons behind such practical performance. In this lecture a comparative analysis of the mechanical and tribological performance of three nanocomposite systems (TiC/a-C, TiBC/a-C, WC/a-C) deposited by magnetron sputtering technique is presented and conclusions are obtained concerning the friction and wear mechanism involved. A deep investigation of the chemical and structural features at the nano-scale is carried out for each family of coatings by many different spectroscopic, microscopic and diffraction techniques. The analysis of the counterfaces by Raman confocal microscopy after the friction tests is used to follow the chemical phenomena occurring at the contact area responsible of the observed friction behaviour. The importance of the evaluation of the free carbon content is highlighted as a key-parameter to understand the tribological properties.

CG-4:IL07 **Hard Protective Thin Films: Mechanical and Tribological Behavior**

M. Fenker*, H. Kappl, FEM Research Institute Precious Metals & Metals Chemistry, Schwäbisch Gmünd, Germany

High hardness combined with a low friction coefficient against a counterpart and high temperature stability (up to several hundreds of degree Celsius) are properties which are of main importance for hard protective thin films. A disadvantage of a lot of developed coating materials is that they fulfill only one or two of the three coating properties. After a short overview on hard protective thin films with the emphasis on hardness, solid lubrication and temperature sensitivity, the paper will discuss the properties of niobium-alloyed nitrogen-containing diamond-like carbon coatings. So far, only the system a-C:H:Nb has been poorly studied and no published data on a-C:H:Nb:N could be found. The coatings have been deposited by reactive magnetron sputtering in an Ar/C2H2/N2 atmosphere. The mechanical (hardness, adhesion) and tribological (pin-on-disc) behavior of the coatings with respect to the C2H2 and N2 flow will be presented. The influence of temperature (up to 500°C in air) on this behavior will be discussed. A coatings hardness up to 2800-3000 HV with a friction coefficient in the range of 0.25 - 0.5 has been measured. An excellent temperature stability was found for a-C:H:Nb:N coatings. Finally results of drilling tests of a-C:H:Nb:N-coated drills will be given.

CG-4:L09 **Boron Nitride Coatings Deposited onto Titanium. Use of an Alternative Ceramization Process**

B. Toury*, H. Termoss, A. Brioude, S. Bernard, P. Miele, Laboratoire des Multimatériaux et Interfaces, UMR 5615 CNRS - Université Lyon 1, Université de Lyon, France; S. Benayoun, Laboratoire de Tribologie et Dynamique des Surfaces, UMR 5513 CNRS - Ecole Centrale de Lyon, Ecully, France

Peculiar properties of h-BN, i.e. high thermal and chemical stabilities even at HT and under harsh environment combined with a lubricant behaviour make h-BN coatings a very interesting solution in non toxic solid lubrication field. Alternatively to usual methods (CVD, sputtering, PLD), BN coatings can also be achieved by the PDCs route. This method i) is easy to implement because it uses liquid-state polymers, ii) is versatile because of the large variety of available precursors, and iii) leads to the preparation of coating in the desired composition and thickness. This route requires the synthesis of liquid or soluble polymeric precursors, its shaping by dip-coating and finally its conversion into ceramic by a suitable treatment. This presentation deals with the preparation of BN coatings from polymeric precursors onto metallic substrates especially titanium (currently used in aeronautic). In that case, the ceramization process is lead via an optical treatment by IR irradiation to overcome the problem of the metal stability at HT (needed in classical process). A summary of the results obtained in term of surface morphology, chemical composition and crystallisation state will be presented. Finally, mechanical properties obtained by nanoindentation will also be discussed.

CG-4:IL10 **WC-Co Coatings Fabricated by Warm Spraying for Wear Protection**

S. Kuroda*, G. Sundararaman, M. Watanabe, M. Komatsu, NIMS, Tsukuba, Ibaraki, Japan; K. Sato, J. Kitamura, Fujimi Inc., Japan

A modified HVOF spraying process called warm spraying has been used to deposit WC-Co coatings. In the process nitrogen gas is mixed with the combustion gas jet in order to lower the gas temperature and control the melting of Co binder phase during spraying. It was found that decarburization and formation of brittle compounds, which are commonly observed in HVOF sprayed WC-Co coatings, could be greatly reduced by lowering the propellant gas temperature. Also, much smoother coating surface, i.e., Ra < 2 microns, could be obtained by using finer powders than those ordinary used for HVOF while avoiding the fatal problem of spitting during spraying. Also the Vicker's hardness over 1500 was achieved by proper combination of feedstock powder and spraying conditions. The results indicate that warm spraying has a great potential to fabricate industrially valuable WC-Co coatings.

CG-4:IL11 **Plasma Assisted Vapor Deposition on Nanostructured Hard Coatings**

Paul H. Mayrhofer, Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Leoben, Austria

Nanostructural design has attracted increasing interest in modern development of hard coatings to improve their performance when used to protect tools, dies, molds, aerospace, and automotive parts. In plasma assisted vapor deposited thin films, the material's nanostructure can be designed during growth or post-deposition annealing treatments. Here we demonstrate the synthesis-structure-property relations of hard ceramic coatings. This is done for single-phase and composition or phase modulated layers. In the latter case, the nanostructure can be designed by choice of the deposition technique, understanding the growth processes taking place on a film surface, either by sequential deposition of layers or by taking advantage of self-organization processes. The influence of alloying elements like Al, B, V, Y, Nb, Hf, and Ta on the phase formation, structure, mechanical and thermal properties of TiN and CrN based coatings is investigated in detail combining experimental and computational studies. Understanding the synthesis-structure-property relations in such model-systems is indispensable to support the massive and collective move in coating industry towards the use of quarternary and multinary nitrides to be followed by carbides, borides, oxides, and oxy-nitrides.

CG-4:L12 **Characterization of Phase Transformation, Micro-structure and Tribological Properties of Ni-B Coating during Heat Treatment**

S. Pal*, N. Verma, V. Jayaram, S.K. Biswas, Indian Institue of Science, Bangalore, India; Y.E. Riddle, UCT Coatings Inc., FLorida, USA

Electroless Ni-B coatings are studied for the influence of heat treatment on crystallization, phase stability, hardness and tribological properties. It is shown from calorimetry and x-ray diffraction that as-deposited amorphous films display a progressive crystallization beginning at ~ 300°C with the formation of Ni3B followed by Ni and then finally, Ni2B at ~430°C. TEM reveals that the microstructure is compositionally modulated in the amorphous state which persists even at 450 C. The microstructure after the onset of crystallization displays nodular regions of ~1-2 microns interspersed with ultra fine banded regions of alternating Ni3B and Ni. Crystalline phases in both regions display a length scale of ~20-50 nm. Isothermal heat treatments at 300 °C display a hardness that rises from 7.5 GPa in the amorphous state to a maximum of ~15 GPa after 5 hours. Further heat treatment brings about a gradual reduction owing to a mixture of coarsening and formation of nickel. Sliding experiments yield friction values as low as 0.04 against steel balls. Tribofilms formed upon sliding are studied using SEM and Raman spectroscopy. AFM is employed to study the frictional response of individual phases in the microstructure and correlate them to the behavior of the overall thin film.

CG-4:L13 **Wear Resistance of AISI M2 Tool Steel Coated with TiN by PVD and Evaluated by the Pin-on-disc Testing**

José Divo Bressan*, Department of Mechanical Engineering - UDESC Joinville, Joinville, SC, Brazil; Fabio Resin, Engenharia de Processos, Ciser, Cia Industrial H. Carlos Schneider, Joinville, SC, Brazil; Rosalba Gerbasi, Istituto ICIS, CNR, Padova, Italia

Present work examines the wear resistance of AISI M2 tool steel coated with TiN by the PVD process from three different suppliers. The coating PVD process has been done, using industrial equipment unit with optimized conditions. The coated layers were measured and characterized. The wear testing by sliding was carried out in a pin-on-disc tribometer whose counter face or discs were SAE 1070 steel of diameter 68 mm, thickness of 2.0 mm and exhibiting average micro-hardness Vickers of 320 mHV0.5. The pins were AISI M2 tool steel heat treated and coated with TiN by PVD in three different coating suppliers; all pins had tip radius of approximately 10 mm. The discs and pins wear behavior were evaluated, using sliding velocity of 0.45 m/s, total sliding distance of 3600 m, normal load of 50 N, controlled room temperature of 26 °C and relative humidity between 40% to 50%. The friction coefficients were measured on-line during testing. From the analysis of the plotted curves of disc and pin cumulative lost volume versus sliding distance and friction coefficient, the various wear rates were calculated and the relationship between the normal load, friction coefficient and wear rate were experimentally examined. The wear mechanisms were also investigated by the friction coefficient.

CG-4:L14 Tribological Behavior of Nanostructured Composite Coatings of Ceramics Manufactured by Suspension Plasma Spraying

G. Darut, H. Ageorges, A. Denoirjean, G. Montavon*, P. Fauchais, SPCTS - UMR CNRS 6638, University of Limoges, Limoges, France

Friction is responsible for about 50% of energy loss in an automotive engine. Reducing friction within an engine is hence a major challenge that has been pursued for numerous years by major automotive companies in collaboration with technical centers. The improvement of new sliding layers is done nowadays following three directions: i) the decrease in the material structure scale; ii) the replacement of the metallic matrix by a ceramic matrix; iii) less lubricated systems. In this context, thermal spraying appears as a pertinent process since it permits processing of a wide range of feedstock, in terms of composition (ceramic, alloys, polymers), architecture (composite powders) and sizes (from micrometer-sized to nanometer-sized). The primary objective of this work is to estimate the effect of the structural scale of plasma-sprayed coatings on some of tribological properties in the dry mode, in particular the friction coefficient. Atmospheric plasma spraying (APS) and suspension plasma spraying (SPS) were implemented to manufacture various coatings, such as Al2O3, Al2O-TiO2, Al2O3-SiC, Al2O3-ZrO2, etc., exhibiting structural scales ranging from 30000 to 30 nm. Sub-micrometer-sized coatings exhibit superior tribological properties compared to conventional micrometer-sized one.

CG-4:L15 Multi-nanolayering Effect on Carbon Films Mechanical Properties and Internal Stress

N. Laidani*, R. Bartali, V. Micheli, G. Gottardi, Fondazione Bruno Kessler, Centro Materiali e Microsistemi, Trento, Povo, Italy; P. Cheyssac, Laboratoire de Physique de la Matiere Condensée, UMR 6622 CNRS, Faculté des Sciences, Parc Valrose, Nice Cedex, France

In this work, the mechanical properties and internal stress of two kinds of amorphous carbon films, one harder than the other, and nano-layered hard/soft carbon films will be presented. Two plasma processes were used for the film synthesis: rf sputtering and plasma assisted chemical vapor deposition. By combining the two plasma processes in sequential film depositions, composite films consisting of periodically stacked hard and soft amorphous carbon layers were produced. Samples structured in 2, 4, 8, 16, 32 layers, with single layer thickness varying from 125 to 7 nm, were prepared and analyzed by transmission electron microscopy and Auger electron spectroscopy. The internal stress was determined from the surface curvature measured using a stylus profilometer. The results show that with decreasing the period width in the multilayer to nanometer scale, the whole structure looses the memory of the soft carbon properties. Positive effects of nanolayering on film mechanical stability are evidenced. We expect that through an accurate architecture design of the carbon multilayer an optimization of the mechanical properties is possible for a wide range of applications.

CG-4:L16 Hydrogen Effect on Structure and Mechanical Properties of Zno Films Deposited by Sputtering in Ar-H2 Plasma

R. Bartali*, I. Luciu, V. Micheli, G. Gottardi, N. Laidani, Fondazione Bruno Kessler, Centro Materiali e Microsistemi, Povo (Trento), Italy

ZnO films were deposited by radiofrequency sputtering with different H2-Ar gas mixtures. During the film deposition excited plasma species were monitored using optical emission spectroscopy. The mechanical properties of ZnO thin films deposited on Si (100) substrates were studied using nanoindentation. The results showed a strong effect of H2 in the gas mixture on film hardness and elastic modulus. Two regimes were observed: at low hydrogen concentrations an increased hardness was obtained with respect to the case of pure argon plasma, while for H2 concentrations higher than 16%, the film hardness was lower. An increased film porosity was also found when H2 is added to the sputtering gas, going from 4% when pure argon was used to a maximum of 16% in the Ar-H2 mixtures. Porosity was estimated from elastic modulus values. In particular, we found a clear correlation between the film porosity and the emission intensity ratio of $H\alpha$ line (656.1 nm) of atomic hydrogen to Ar (4p'-4s') line at 750.4nm.

CG-4:L17 Mechanical Reliability of ZnO Thin Films Used in Glass Stacking Applications

F. Conchon, P-O. Renault, P. Goudeau*, E. Le Bourhis, PHYMAT - UMR 6630, Poitiers, France; E. Sondergard, E. Barthel, S. Grachev, SVI - UMR 125, Aubervilliers, France; E. Gouardes, V. Rondeau, R. Gy, SGR, Aubervilliers, France; R. Lazzari, J. Jupille, INSP - UMR 7588, Paris, France; N. Brun, LPS - UMR 8502, Orsay, France

ZnO is a material of technological importance for, among other things, its practical and potential applications in glass stacking as a UV spectrum filter and can provide other promising technological applications thanks to its adjusting photoluminescence properties. Unfortunately, large compressive intrinsic stresses arising during the deposition process can induce changes of the physical properties and promote delamination or failures of the ZnO films. The control of their mechanical reliability can then be achieved by an in depth comprehension of the residual stresses build up or relaxation mechanisms occurring in the films in relation with the material structure. In this communication, we show that the residual stresses are strongly correlated to the microstructure of the films. In particular, we will demonstrate thanks to X-ray diffraction ($\sin^2\Psi$ analysis) and in-situ curvature measurements that residual compressive stresses can be relieved by tuning the point defects concentration of the films. This can be achieved by adjusting sputter-deposition parameters such as oxygen partial pressure and annealing temperature/atmosphere. This work is done in the framework of a French ANR project named Merethif.

CG-4:IL18 Nanostructured Thin Coating Architectures for Environmental Technology Applications

Vasco Teixeira*, Joaquim Carneiro, Pedro Carvalho, University of Minho, Physics Department, GRF-Functional Coatings Group, Campus de Azurém, Guimarães, Portugal

With the development of nanotechnology in various areas of materials science the potential use of novel surfaces and more reliable materials by employing nanocomposite and nanostructured thin films in energy, mechanical, tribology, medicine and food packaging among many others, can be considered. Nanostructured materials and thin films offer the potential for significant improvements in nano-engineering and opto-electronic properties based on improvements in physical, chemical and nanomechanical properties resulting from reducing microstructural features by decreasing the grain size of a material to the nanometer range compared to current technological materials. The self-cleaning of super-hydrophobic micro- to nano-structured surfaces was first observed to be a property of some plants (e.g. leaves of Lotus). Hydrophobic-hydrophilic properties and photocatalytic behavior of nanoscale materials and nanocoatings is receiving growing interest in nanotechnology research, given the foreseeable introduction of commercial products into markets. Nanostrucutured thin films can be tailored in order to show easy-release, hydrophobic and anti-microbial properties. Nanocomposite and graded thin films for environmental technologies, energy systems and smart surfaces will be presented.

CG-4:IL19 Computational and Experimental Investigation to Understand the Adaptation Mechanisms of Chameleon Coatings

S.M. Aouadi*, D. Stone, A. Abu-Nada, Department of Physics, Southern Illinois University, Carbondale, IL, USA; C. Muratore, A.A. Voevodin, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, Ohio, USA

Effective lubrication over a broad range of ambient temperatures and atmospheres is one of the most challenging problems in tribology, and has been a road-block to innovation in aerospace, tooling and material forming, automotive, military, and nuclear power industries for decades. Recently, a series of double metal oxide compounds, composed of a transition metal phase and a soft metal phase, have been investigated as solid thin film lubricants for applications with broad ranges of operational temperatures (25-1000 °C). The goal of this paper is to give an overview of the computational and experimental work that is currently being conducted to understand the tribological properties of double metal oxides at high temperature. The modeling effort, based on density functional theory simulations, aims to illustrate the structural, chemical, thermal, and mechanical properties of these materials. It will also be used to provide guidance on unexplored material combinations expected to demonstrate low shear stress for easy shearing at contact interfaces and long-term temperature stability. Several double metal oxides have been synthesized and their chemical, physical, and frictional properties were characterized in situ at different temperatures. Finally, we discuss incorporation of these single phases that form effective double metal oxide lubricant compounds into the design of adaptive "chameleon" coatings, that automatically adjust their surface chemistry and structure with the working environment to reduce friction and wear. The new designs of adaptive coatings that will be discussed include: (i) nanocomposite; (ii) nanotextured; and, (iii) nanotube-based designs.

CG-4:L22 Pros and Cons of Three Potential Easy-to-clean Coatings on Glazed Surfaces

M. Piispanen*, L. Hupa Process Chemistry Centre, Abo Akademi University, Turku, Finland

Advantages and disadvantages of potential coatings on glazed surfaces manufactured via three different approaches were studied. The surfaces were coated with i) a soil-repelling fluoropolymer film applied at room temperature, ii) a titania film applied with sol-gel technique and matured at 500 °C, iii) titania nanoparticles applied by liquid flame spraying on surfaces at 600-800 °C. The effects of the coatings on the surface appearance, roughness, water contact angle, soil attachment and removal were measured. Chemical and mechanical durability of the surfaces were compared. The fluoropolymer coating was easy to apply, but it degraded in alkaline environments. Its mechanical durability was poor. Application and maturing of the sol-gel titania coating was rather complicated. The coating showed good chemical and mechanical durability. The coating was also self-cleaning. Titania nanoparticles applied by flame spraying can be implemented easily in the firing cycle. Due to a low thickness the self-cleaning properties of this surface were not as good as the properties of the sol-gel coated surfaces. All coatings enhanced easy-to-clean properties. The coating should be chosen according to the conditions at which the surfaces will be used to guarantee their long-term performance.

CG-4:IL23 Damping Properties of Hard Coatings for Engine Applications

Peter J. Torvik, Professor Emeritus, Air Force Institute of Technology, Xenia, OH, USA

As the integrated blade-disk assemblies being developed for use in gas turbines lack frictional interfaces, other means of adding the dissipation necessary if blade fatigue at high cycles (HCF) is to be avoided. The damping ability of blade coating materials also serving another function, such as protecting the substrate against wear and/or erosion, or as a thermal barrier coating, are of high interest. But reported measurements for ceramics and magnetoelastic metals shows that these suggested coatings alone do not provide the desired levels of damping. It has been found, however, that significant increases in the damping of plasma sprayed ceramics result from the inclusion of a viscoelastic material, with indications that the resulting coating may be tailored for a specific temperature range by selection of the high-damping component. Vacuum infiltration of a viscoelastic component into a plasma-sprayed ceramic has been found to raise the dissipation to desired levels at temperatures in the range of 90-120 C, and co-spraying a mixture of ceramic and enamel has been shown to lead to extremely high damping in the transition range of the enamel, typically in the range of 550-800 C. A suitable additive for intermediate temperatures, such as 250-450 C, remains to be identified.

CG-4:IL24 Correlation Between Mechanical Properties and Different Coating Architectures

S.J. Bull, Chemical Engineering and Advanced Materials, Newcastle University, Newcastle Upon Tyne, UK

In most coating applications damage resistance is controlled by the mechanical properties of the coating, interface and substrate. However, for electronic and optical applications the design of coating-substrate systems has been controlled by their functional properties except in a few cases where the mechanical response of the system has been used to enhance functional properties, as in the case of strained silicon/SiGe microelectronic devices where tensile strain has been used to enhance mobility and increase device speed. As coatings become more complex, with multilayer and graded architectures now in widespread use, it is very important to obtain the mechanical properties (such as hardness, elastic modulus, fracture toughness, etc.) of individual coating layers for use in design calculations and have failure-related design criteria which are valid for such multilayer or multicomponent systems. This presentation will discuss the assessment of the mechanical properties of very thin coatings and how these are used for mechanical design of functional devices. Single, multilayer, superlattice and nanocomposite coating architectures will be considered and the role of grain size, shape and orientation in the mechanical response of coatings and nanostructures will be highlighted.

CG-4:IL25 Adaptive Multifunctional Nanocomposite Coatings for Aerospace Applications

A.A. Voevodin*, C. Muratore, Air Force Research Laboratory, Thermal Sciences and Materials Branch, Wright-Patterson Air Force Base, OH, USA

Air and space applications involve a variety of mechanisms that need to operate reliably in extreme environments, including high thermal and mechanical loads, oxidizing and corrosive atmospheres, or high vacuum. The operating conditions span from cryogenic temperatures from liquid fuels of rocket engines to high temperature oxidizing environments of jet engines. Satellite mechanisms designed for space are tested on Earth under ambient (e.g., humid) environmental conditions. Aircraft leading edges, rotor-blades and compressor airfoils of jet engines need protection against high velocity sand erosion as well as corrosive environments. Nanocomposite and multilayer coating architectures have been developed to confront these challenges with self-adaptation mechanisms responding to temperatures, environments, and mechanical loading. Such smart adaptive coatings offer multifunctionality by providing low friction and wear, corrosion protection, management of heat flow at contact interfaces, and automatic reporting on the state of the surface wear. Conclusions about potential impact and future directions of adaptive multifunctional nanocomposite materials initially explored for aerospace, but with applications for tool, automotive, and other industries, will be presented.

CG-4:L26 Synthesis of TiO2 Thin Films by Ink-jet Printing from Water Based Sol-gel Precursors

M. Arin*, P. Lommens, I. Van Driessche, Department of Inorganic and Physical Chemistry, Ghent University, Ghent, Belgium

TiO2 thin film coatings prepared by chemical solution deposition methods are attractive because of simple production of large area and high purity films. Preparation of these materials at lower temperatures without toxic substances or organic solvents is new in this area and leads to cheap, safe, and environmentally friendly production processes. This study focuses on the synthesis, deposition and characterization of TiO2 thin films obtained by ink-jet printing of water based precursor solutions on glass substrates. Controlled hydrolysis of the alkoxide precursor is achieved by adding complexing agents such as acetylacetone, citric acid, and triethanolamine prior to water addition (>70 vol% H2O). The transparency, thickness and photocatalytic activity of the films were evaluated. The characterization of the resulting TiO2 films clearly showed that transparent, thin, dense oxide films were obtained at 450-650 °C. The anatase TiO2 phase was formed at 450 °C whereas at temperatures higher than 650 °C both anatase and rutile TiO2 crystalline phases were formed. This approach for the production of TiO2 layers provides us with a completely non-toxic and extremely flexible route towards the manufacturing of transparent, dense, photocatalytically active ceramic thin films.

Poster Presentations

CG:P01 Application of SEM/STEM and XPS to Tests on Pt Distribution in Al2O3 Films Obtained by Oxidising FeCrAl Steel Foil Coated with Pt-Al Nanofilms

Kazimierz Reszka*, Institute of Mechatronics, Nanotechnology and Vacuum Technique, Koszalin University of Technology, Koszalin, Poland; J. Rakoczy, Institute of Organic Chemistry and Technology, Cracow University of Technology, Cracow, Poland; J. Morgiel, Institute of Metallurgy and Materials Science, PAS, Cracow, Poland

Good dispersion of active catalytic elements, their uniform distribution on the carrier's surface and availability for neutralised combustion gases are key factors that determine the usability of catalyst cartridges for automotive catalytic reactors. By examining the morphology of oxide films, with SEM/STEM method, obtained by oxidation of foil coated with Pt/Al two-layered system (like laminate), where an Al nanofilm is situated between steel foil and a Pt nanofilm, one can observe forked and plate whiskers growing directly of substrate. Oxide films obtained from Pt+Al composite nanofilms were formed differently (where components are intermixed). These films are marked by chaotic, mutually penetrating fine equiaxed solids and whiskers. XPS examinations revealed the presence of signals deriving from Pt located on the specimen surface, which confirmed the accessibility of potential components of combustion gases to it. In case of composite nanofilms the grain system obtained in the course of deposition contributed to good Pt grain refining, and due to that mostly particles from 3 to 9 nm in conventional diameter were formed. Direct contact between Pt particles and Al particles caused the partial occlusion of Pt particles with oxide in the process of Al oxidation to be effected.

CG:P02 A Chemometric Study of Alumina/PEEK Suspension Prepared for Electrophoretic Deposition of Multifunctional Coatings

M.F. De Riccardis, V. Martina*, D. Carbone, ENEA Brindisi Research Centre, Brindisi, Italy

Electrophoretic Deposition (EPD) is a useful electrochemical method used to produce coatings, principally made of ceramics. Recently this technique has also been used to obtain coatings based on polymer and composite materials. Amongst polymer materials, poly(etherether-ketone) (PEEK) is particularly interesting as a high-quality engineering thermoplastic. Composites based on PEEK containing ceramic particles have a great significance for the possible applications in aerospace, electronic, automotive and biomedical fields. As coatings, inorganic-PEEK composites can give functional properties to a surface depending on the characteristics of the ceramic phase. During our work, Alumina particles were added to a PEEK suspension thus obtaining an improved wear resistance material. When hydroxyapatite (HA) was added, a useful biocompatible material was obtained. PEEK suspensions, suitable for EPD process and containing different concentration of Al2O3 and HA particles, were prepared in alcoholic media. The quality of the suspensions were studied by means of zeta potential and grain size measurements. The comparison amongst the different suspensions was carried out by using statistical and chemometric tools.

CG:P03 ESR Study of Elements Added-DLC Films Deposited by PBII and RF-CVD Methods

N. Moolsradoo*, H. Sato, S. Watanabe, Nippon Institute of Technology, Miyashiro-Machi, Minami Saitama-Gun, Saitama, Japan

DLC films exhibit a wide range of spin densities obtained from ESR measurements, and the spin density has often been used as one of the important parameters that determine the characteristics of the DLC films. The aim research was to study the effects of element content on the spin density and their relation to the changes in the structure of the DLC films prepared by PBII and RF-CVD methods. The Raman spectra known to be the most definitive criteria for characterizing the structure of DLC films is also represented along with the ESR measurements. PBII and RF-CVD methods were utilized to prepare three different elements including hydrogen, sulfur, and fluorine added-DLC films on Si (100) substrate. The DLC films were deposited from gaseous mixtures of C2H2:H2, C2H2:SF6, and C2H2:CF4, at three different flow rate ratios, 1:4, 1:2, and 2:1. The RF power was set to 300 W, and thickness of all films was 500 nm. The bias voltages of PBII method were set to different values of 0 kV and -5kV, at the deposition pressure was set to 2 Pa, 3 Pa for RF-CVD method. For hydrogen added-DLC films prepared by RF-CVD were observed that the ESR signal with a g-value decreased from 2.00344 to 2.00317. The spin density decreased, while the ID/IG ratio increased, with increasing hydrogen contents.

CG:P04 Corrosion Resistance of Titanium Aluminide Layers on Two Phase (a+b) Ti6Al4V Titanium Alloy

R. Sitek[1]*, J. Kaminski[1], M. Pisarek[2], H. Matysiak[3], K.J. Kurzydlowski[1], [1]Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland; [2]Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland; [3]Research Centre for Functional Materials, Warsaw University of Technology, Warsaw, Poland

Surface engineering methods, in particular Chemical Vapour Deposition (CVD), are used to improve the surface properties of titanium alloys such as microhardness, abrasive wear and creep-resistant without compromising their good corrosion resistance at the room temperature. In the present paper, the results are reported of the investigations which show the microstructure and corrosion resistance of Ti-Al diffusion layers consisting of two-phase (a+b) on the Ti6Al4V substrate. These layers were produced by CVD method in aluminium chloride (AlCl3) mixed with argon atmosphere at the temperature of 700 °C. Surface analytical techniques such as SEM, EDS and XPS were employed to characterize the morphology and chemical composition of the layer. XRD and TEM were used to examine the phase composition of the coating. The corrosion resistance of Ti-Al/Ti6Al4V samples was investigated by potentiodynamic polarization method in 0.1M Na2SO4 and 0.1M H2SO4 solutions at the room temperature. The resistance to high temperature of the coatings at atmospheric pressure was tested by applying 24-hours cycles at 650 °C. The results indicate that the layers produced on the Ti6Al4V titanium alloy exhibit a very good adhesion combined with exceptional corrosion resistance-especially at high temperatures.

CG:P07 Slurry Coating of Environmental Barrier Coating (EBC) on Silicon Carbide Based Material

F. Bezzi*, P. Fabbri, A. Brentari, C. Mingazzini, E. Burresi, S. Sangiorgi, ENEA, Engineering of Components and Processes Section - Faenza Research Centre, Faenza, Italy

In combustion environments, as gas turbines for power generation, silicon carbide (SiC) and its composites are attractive due to their high strength, high creep resistance and good thermal shock resistance. The major drawback of SiC based ceramics is the susceptibility of the silica protective scale to volatilization by steam, oxygen and alkali salts at high temperature. In order to increase the component lifetime EBC systems based on ceramic oxides are used to improve corrosion resistance due to their high chemical stability. In this work, mullite and barium-strontium-aluminosilicate (BSAS) coatings were deposited by slurry dip coating on SiC substrates. Slurries were prepared by suspending commercial powders in water, using appropriate dispersants. Substrates were dipped into the slurry and subsequently dried and heat treated at high temperature to promote densification. The most significant characteristics of the slurries, like powder concentration, particle size distribution and viscosity, and dip-coating parameters, like substrate withdrawal speed, solvent evaporation and thermal treatment conditions, were controlled. SEM observations were carried out to investigate the microstructure of the obtained coatings and to evaluate crack formation, adhesion and porosity.

CG:P08 Formation of an Alumina-containing Scale for the Surface Protection of TiAl Alloys and Ti Against Environmental Degradation at Elevated Temperatures

R.A. Yankov*, A. Kolitsch, F. Munnik, J. von Borany, Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf , Dresden, Germany; A. Donchev, M. Schütze, Karl-Winnacker-Institut, High-Temperature Materials, DECHEMA e.V., Frankfurt am Main, Germany

Ti and TiAl alloys are lightweight materials that hold great promise for advanced aerospace, automotive and power generation applications. They are, however, limited in applicability by their poor oxidation resistance above 600 °C. We have developed a process for enhancing the high-temperature oxidation resistance of these materials. For TiAl, the process involves a single step, i.e. plasma immersion implantation (PIII) of fluorine relying on the so-called “halogen effect”. Optimum conditions have been established under which the alloys acquire a stable, adherent and highly protective alumina scale upon subsequent high-temperature oxidation in air. The extent of oxidation protection has been evaluated by testing F-implanted TiAl samples at temperatures up to 1050 °C. Results from characterization by elastic recoil detection, X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray analysis have proven the possibility of forming a protective alumina scale on both laboratory coupons and components such as turbine blades and turbochargers. In the case of Ti, surface processing involves two steps, i.e. Al enrichment of the Ti near-surface, and introduction of F by PIII. The Ti samples so modified have shown marked environmental stability at temperatures up to 700 °C.

CG:P09 Advances in the Field of New Smart Thermal Barrier Coatings

F. Ansart*, J. Fenech, L. Pin, J.P. Bonino, P. Lours, Y. Le Maoult, Université Paul Sabatier, Toulouse, France

This paper deals with the development of a new synthesis technique for functional materials such as Yttria or Rare Earth Stabilized Zirconia (YSZ or RE-SZ) in the field of thermal barriers coatings. Currently, Thermal Barrier Coatings (TBCs) are manufactured by dry route technologies (EB-PVD or plasma spray) but such methods are directional and often require costly investments and complicated operations. For these applications, we have developed sol-gel routes, which are nondirectional methods, to prepare, by suitable chemical modifications, nanocrystalline materials with a controlled morphology. The main advantage of this method is to decrease the crystallization temperature, much lower than the conventional processes, allowing the synthesis of reactive substituted zirconia powders with nanometric particles size. In this study, several new architectures for thermal barrier coatings have been carried out in order to optimise their functional properties : thermo-mechanical accommodations compared to conventional processes evaluated by cyclic oxidation tests, with and without thermal gradient to investigate spallation mechanisms and overall TBC durability but also luminescence properties by the incorporation of suitable rare earths.

CG:P10 Optimisation of the Ceramic Phase for Ceramizable Silicone Rubber Based Composites

Zbigniew Pedzich[1]*, Krzysztof Haberko[1], Dariusz M. Bielinski[2, 3], Jan Dul[2], [1]AGH University of Science & Technology, Dept. of Advanced Ceramics, Cracow, Poland; [2]Division of Elastomers & Rubber Technology, Institute for Polymers & Dyes Technology, Piastow, Poland; [3]Institute of Polymers, Technical University of Lodz, Lodz, Poland

Flame resistance of electrical cable covering insulation is very important from the safety point of view of people using means of transport, visiting shopping centers, sport halls, theatres or cinemas. Metal rods in protective covering make the main part of electrical circuits, responsible for distribution of electricity in cars and planes, providing power supply for elevators or fire-fighting systems. Material used nowadays, based on silicone rubber or PVC is incombustible, but the problem concerns its mechanical durability under flame, maintaining circuit integrity and energy supply during fire, indispensable to secure time for evacuation or emergency landing. Integrity of electrical cables can be obtained by application of covering insulation made of polymer composites ceramizing at high temperature arising during fire. The paper presents results of investigation on optimization of ceramic phase using in mentioned composites.

CG:P11 Influence of Thermal Annealing in the Bonding States and Structural Arrangements of Multifunctional Ti(C,O,N) Coatings

Cacilda Moura[1]*, Luís Cunha[1], Jean-Marie Chappé[2], Filipe Vaz[2], M.C. Marco de Lucas[3], L. Imhoff[3], O. Heintz[3], [1]Physics Department, University of Minho, Campus de Gualtar, Braga, Portugal; [2]Physics Department, University of Minho, Campus de Azurém, Guimarães, Portugal; [3]Institut Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, Dijon Cedex, France

This work reports on the study of thermal stability of dark decorative Ti(C,O,N) thin films produced by reactive magnetron sputtering. The thermal resistance and evolution of structural and physical properties were studied by performing annealing experiments for temperatures varying from 600 to 1000 °C. In order to study the effect of the thermal treatments on the evolution of composition, Rutherford backscattering spectrometry experiments were conducted in both as-deposited and annealed samples. Furthermore, and in order to study the influence of the annealing experiments and the correspondent composition variations on the types of bonds that were developed, a set of X-ray photoelectron spectroscopy were carried out. For the fcc-type samples, it was shown that with the thermal treatment, some loss of non-metallic elements occurs, which affected the structural arrangements, namely in the formation of a nano-composite-type structure, where nano-grains (cubic lattice type, with Ti vacancies and mixed O+N) are dispersed in a carbon amorphous matrix. The presence of this carbon amorphous matrix, which revealed to be one of the main parameters that control the film's behaviour, was confirmed by both XPS and Raman measurements.

CG:P12 Chromium Nitride and Silicon Doped Chromium Nitride Coatings Produced by Magnetron Sputtering: Effects of The Nitrogen Flow on the Structure and Mechanical Properties

L. Cunha*, C. Moura, Physics Dept., University of Minho, Braga, Portugal

Chromium nitride and silicon doped chromium nitride thin films have been deposited by r.f. reactive magnetron sputtering. The effect of processing parameters and of the addition of silicon on the chromium nitride matrix in the films structure and mechanical properties has been investigated systematically. The characterization of the coatings was performed by X-ray diffraction (XRD), and nano-indentation experiments. These studies allow analyzing the crystalline phases, crystal orientation/ texture, crystallite size, the mechanical properties and the relations between the characteristics of the films. Increasing the nitrogen partial pressure in the working atmosphere produces changes from a body-centered cubic (bcc) Cr structure, to hexagonal Cr2N to face-centered cubic (fcc) CrN microstructure. With the introduction of Si, the CrN (111) preferred orientation is maintained. For the films with a dominant Cr2N phase the hardness has a relative maximum (42 GPa). The crystallite size is around 5 nm. The highest hardness was measured for a coating with dominant CrN phase (45 GPa) with a crystallite size around 18 nm.

CG:P13 Study of the Films of Secondary Structures on the Interface in Sliding Friction Pairs

I.I. Kurbatkin*, A.Yu. Ishlinsky, Institute for Problems in Mechanics, Russian Academy of Sciences, Moscow, Russia

The films of secondary structures formed on a surface friction pair as a result of mass transfer and interactions with environment, make essential impact on tribological properties. The structure, roughness and composition of the interface are studied for following sliding friction pairs: shoes from aluminum antifriction alloys and a roller from high-strength cast iron. The tests were carried out with the shaft-shoe scheme simulating critical conditions of the engine operation in the start-stop mode and for wear resistance. The structural mechanism of mass transfer between the shoe and roller is analyzed. On the interface and subsurface layer an active tribological region is formed which has considerable structural and chemical heterogeneities. The analysis of the interface composition showed that components from shoe (Sn, Al, O, C,N) are actively transferred onto the roller, and Fe, C and O - onto the shoe. As a result of this the so-called tribolayer is formed on contact surface, which can act as lubricant so lead to formation of micro- and macro reliefs. Dependences of the amount of the formed lubricant on the main material characteristics (yield points of the phase, their size and distribution) are obtained by modeling. Calculated data correspond to experimental results.

CG:P14 Amorphous Si:C:H and Si:N:H as Antireflective and Protective Coatings

B. Swatowska*, T. Stapinski, S. Zimowski, AGH University of Science and Technology, Krakow, Poland

Hydrogenated amorphous silicon-carbon a-Si:C:H and hydrogenated amorphous silicon-nitride a-Si:N:H thin films have been deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) at 13.56 MHz in SiH4+CH4 and SiH4+NH3 gaseous mixture with changeable CH4 and NH3 contents and various deposition time. The films were deposited onto crystalline silicon and multicrystalline silicon substrates. The process parameters were chosen to obtain the films of optimal energy gap, refractive index, and low effective reflectivity for optoelectronic and mechanical applications. PECVD method allows production of films of desired properties. Optical characterization of films was done by PERKIN-ELMER spectrophotometer. Film structure and morphology was examined by Fourier Transform Infrared Spectroscopy FTIR, Scanning Electron Microscopy and by profilometry. The investigations revealed that both materials have optical properties suitable for application in solar cells as antireflective coatings. The friction coefficient of silicon substrates modified by a-Si:C:H and a-Si:N:H films detected by Pin-On-Disc Tester decreases. It was observed that the wear resistance of the substrates increases. The investigations indicated that these films have promising properties for surface protection.

CG:P15 Influence of Inorganic Sealant in Hot and Cold Erosive Wear in Plasma Sprayed Alumina Coating

J. Vicenzi*, A.S. Takimi, R. Brambilla, C.P. Bergmann, Federal University of Rio Grande do Sul, Porto Alegre, RS, Brazil

Plasma sprayed alumina coating is successfully used in many industrial applications to promote wear and corrosion resistance and thermal barrier. The high porosity that remains after sprayed and small wear resistance is the critical factor in this coating. The sealants are used to diminish the open pores and superficial micro-cracks effect. The plasma sprayed alumina coating samples were divided in two groups: i) impregnated by inorganic sealant (Al2(OH)3 + H3PO4 based) and thermal treated; ii) remain as deposited. Erosive wear tests were carried out in an apparatus based in ASTM G76. The samples were subjected to a erodent flux, with impact angles of 30° up to 90°, at a velocity of 50m/s and temperatures of 25 °C up to 800 °C. The samples were characterized by microstructure, mechanical properties and erosive wear rate. The results have shown that erosive wear rate of alumina impregnated coating is lower than without the sealant. The sealed alumina coating presents higher mechanical properties; improved microstructural characteristics and the sealant promote better lamellae contact, as can be observed by less sharpness in pits formation of microstructure.

CG:P17 Low-temperature Synthesis of TiO2 Coatings by Sol-gel Chemistry

M. Cuadrado Gil*, P. Lommens, I. Van Driessche, K. De Buysser; Universiteit Gent, Gent, Belgium

TiO2 ceramic coatings can be used as self-cleaning, anti-corrosion coatings on stainless steel. In this research, these multifunctional coatings are prepared by dip coating of the substrates in an aqueous sol-gel precursor solution. The use of environmentally friendly reagents and a mild temperature program together with the straightforward scalability renders this deposition route suitable for industrial partners. We developed a stable, water-based precursor solution system containing low amounts of organics. The hydrolysis of the alkoxide-precursors is controlled by addition of complexing agents. We optimized solution parameters such as concentration, metal to complexant ratio, pH, organic solvent content, etc based on the information obtained from high-throughput experimentation. The finally selected precursor solutions are fully characterized and used to deposit a TiO2 thin layer on stainless steel substrates.

CG:P18 Effect of Methane Flow Rate on the Microstructural and Mechanical Properties of Silicon Carbide Thin Films Deposited by Reactive DC Magnetron Sputtering

Erdem Baskurt*, Tolga Tavsanoglu, Onuralp Yucel, Department Of Metallurgical & Materials Engineering, Istanbul Technical University, Istanbul, Turkey

Silicon carbide thin films have attracted much attention in recent years because of their excellent mechanical and thermal properties, such as high hardness, good wear-resistance, high thermal conductivity and high chemical inertness at high temperatures. In this study, SiC films were deposited by reactive DC magnetron sputtering of high purity (99,999 %) Si target. Films with different compositions were obtained by varying the CH4 / Ar proportion in the sputtering gas (0-50 %). 3 types of substrates, AISI M2 grade high speed steel, glass and Si (100) wafer were used in each deposition. Films were deposited without external heating and a negative bias voltage (Vb) of 50 Volt was applied to the substrates. The effect of different CH4 flow rates on microstructural properties were characterized by cross-sectional FE-SEM observations. Chemical composition of SiC films was measured by EPMA/WDS analyses. Microhardness measurements were used to determine the hardness values and "pin-on-disc" tests were realized to elucidate the tribological properties of the coatings.

CG:P19 Development, Accelerated Ageing and Osteoconduction Study of Ceria Stabilized Zirconia in Simulated Body Fluid

Ajoy Kumar Pandey*, Koushik Biswas, Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Kharagpur, India

Ceria stabilized zirconia (CSZ) powder was synthesized by coprecipitation method. Composition for full stabilization, sintering schedule for complete densification and grain size were optimized. In vivo stability of developed material was predicted through in vitro ageing test carried out under Simulated Body Fluid (SBF) at 134 °C/0.2 MPa for 100 h (1h in vitro = 3-4 yrs in vivo). Biocompatibility of the material was inferred from formation of hydroxyapatite on the surface of the material during osteoconduction study at 37.5 °C(ISO 6474-2) for 1 month under SBF. Average hardness of sintered CSZ samples was estimated to be 945HV20 which is 35% higher than the reported values. After hydrothermal treatment some grain pull outs, probably due to tetragonal to monoclinic phase change, were observed on the surfaces and hardness value drops to 832HV20. Monoclinic phase contents were estimated by Rietveld analysis of XRD patterns before and after the hydrothermal treatment. Fretting wear at 50N load in ball on flat geometry was carried out for 100000 cycles and lowest specific wear rate was estimated to be 4.28 *10-9 mm3/Nm. The main mechanisms for wear were found to be grain pull out, microcrack formation, surface fatigue and successive abrasion of wear debris.

CG:P21 Structural and Chemical Investigation of RF Magnetron-sputtered Ti-B-N and B-N Hard Coatings

Serim Ilday[1]*, Erman Bengu[2], [1]Graduate Program of Materials Science and Nanotechnology, Bilkent University, Ankara, Turkey; [2]Department of Chemistry, Bilkent University, Ankara, Turkey

Tribological properties of B-N containing hard films are of much importance for industrial applications and have been studied for some time. However, the effect of the substrate bias on the microstructure has been seldom investigated. Here, we show that the substrate bias is indeed instrumental in determining the film properties by way of altering the microstructure. The effect of target power, N_2 gas ratio, substrate temperature and bias have been investigated for Ti-B-N and B-N coatings deposited on low-carbon steel and Si (100) substrates. Our data indicate that the observed phases at lower RF power levels are a mixture of h-TiBN and TiN, while for higher RF power levels we observed the hard e-BN phase in these films. We find that by floating the substrate voltage e-BN phase can be obtained at lower target powers and N_2 gas ratio, even though structure is associated with high powers and N_2 gas ratio. Similarly, when comparable deposition conditions were used with an h-BN target, we observed the evidence for the same e-BN phase in these films, as well. The nanohardness values of both Ti-B-N and B-N films were measured in excess of 35 GPa. In order to understand the nature of the e-BN phase, we have done detailed TEM analysis on these films. Furthermore, we have also done pin-on-disc tests at elevated temperatures to understand the high-temperature tribological properties of the films.

Symposium CH

ADVANCES IN ELECTRICAL, MAGNETIC AND OPTICAL CERAMICS

Oral Presentations

Session CH-1
Dieletric and Microwave Materials

CH-1:IL01 Microwave Dielectric Ceramics for Resonators and Filters in Mobile Phone Networks

Ian M. Reaney, Department of Engineering Materials, Sir Robert Hadfield Building, University of Sheffield, Sheffield, UK

Temperature stable, medium permittivity dielectric ceramics have been used as resonators in filters for microwave (MW) communications for several decades. The growth of the mobile phone market in the 1990's led to extensive research and development in this area. The main driving forces were the greater utilisation of available band width which necessitates extremely low dielectric loss (high quality factor), an increase in permittivity so that smaller components could be fabricated and, as ever in the commercial world, cost reduction. Over the last decade a clear picture has emerged of the principle factors which influence MW properties. This presentation reviews these basic principles and gives examples of where they have been used to control microwave properties and ultimately develop new materials.

CH-1:IL02 Carbon Nanotube Cathodes as Electron Sources for Microwave Amplifiers

P. Legagneux, Nanocarb, Thales-Ecole Polytechnique, Palaiseau, France

Compared to solid state amplifiers, vacuum amplifiers such as travelling wave tubes (TWTs) offer higher powers, higher frequency operation, an excellent power yield (~70%) but are bulky and heavy. TWTs uses thermionic cathodes that emit a continuous electron beam. It has been known for a long time that the integration of cold cathodes delivering a modulated electron beam is a solution to reduce the size and weight of these tubes. For this purpose, arrays of vertically aligned multi-walled carbon nanotubes (MWCNTs) have been extensively studied. MWCNTs are arguably the most stable and robust cold field emitters known. A stable emission current of 100-200 µA per individual MWCNT has been demonstrated and arrays of MWCNTs are able to emit large current densities (>1 A/cm2). To allow high frequency and large bandwidth modulation of the emitted beam, we have proposed the concept of CNT photocathode. This photocathode is an array of MWCNTs, each CNT being associated with one semiconducting p-i-n photodiode. Schematically, the photodiode acts as a current source and delivers a current which is proportional to the illumination power. First experiments concerning the operation of a CNT cathode in a TWT and also concerning a CNT photocathode operating in the GHz range will be presented.

CH-1:IL04 Miniature Ceramic Antennas for Wireless Applications

Z.D. Milosavljevic, Pulse Finland Oy, Kempele, Finland

In recent years, as the size of wireless devices, such as mobile phone, has decreased, it is becoming necessary an antenna to be mounted in a small area. This requires reduction in the size and thickness of the antenna, and thus degrades bandwidth and efficiency. Plated metal on ceramics ("chip antennas") can provide high performance for narrowband antenna applications. They have traditionally been used in handset connectivity or peripherals (GPS, Bluetooth, Wi-Fi etc). However, they are becoming very competitive even for the main antenna applications (GSM, WCDMA, CDMA etc). This paper will present very efficient, new, cutting edge miniature ceramic antenna solutions. They are based on using both single ceramic/chip antenna and multiple chips forming a distributed antenna system. Very efficient antenna designs in conjunction with properly selected matching circuits are giving low-loss miniature structures. Additional increase in the effective bandwidth of antenna system is achieved by using antenna band switching/tuning. The antenna switching is realized using extra switching circuits in proximity to it and being electrically coupled the radiator. Those switching circuits are based on using switching element that can be realized in different technologies as GaAs, CMOS, MEMS etc.

CH-1:IL05 Local Structure in Perovskite-like Dielectrics

I. Levin, Ceramics Division, NIST, Gaithersburg, MD, USA

Perovskite-structured oxides account for a large share of the market for electronic ceramics. Local atomic arrangements in complex perovskites and their solid solutions frequently deviate from those described by the average crystallographic positions. In many cases, such local deviations control functional properties of perovskites and, therefore, establishing comprehensive structure-properties relations requires accurate knowledge of the local structure details. However, quantitative characterization of local atomic displacements and chemical short-range order in these materials remains a challenge. In this talk, we will discuss studies of local structures in several perovskite dielectrics using combined input from X-ray absorption spectroscopy, neutron total scattering, and electron diffraction.

CH-1:IL06 Aerosol Deposition Process for Fabrication of Dielectric Layer

J. Akedo*, D. Popovici, M. Suzuki, Y. Imanaka, T. Tsurumi, AIST, Tsukuba, Ibaraki, Japan

Aerosol deposition (AD) is a novel ceramic coating method using room temperature impact consolidation (RTIC) phenomena for ceramic fine powder. This method has a wide range potential for fabrication of integrated micro devices and novel nano composite materials. This paper reviewed the development of dielectric layers fabricated by AD method at first. BaTiO3 and BaSrTiO3 system thin and thick films were successfully fabricated on Cu substrates at room temperature by employing an AD method. Their dielectric permittivity and dielectric loss tangent were enhanced to approximately 90~120 and 1~1.5% at 100 kHz, respectively. After annealing at 300 °C in air, their dielectric permittivity also increased up to approximately 200~300. Finally, we could obtain the capacitance density of 300 nF/cm2 for the ADM-derived BaTiO3 film. As-deposited BST (x=0.6) film at R.T. even showed a tunability of 15%. At the BST(x=0.6) film annealed at more than 400 °C, a high tunability of 30% can be obtained at an applied electric field of 150 kVcm-1. Embedded capacitors and RF filters were also fabricated.

CH-1:IL07 Reducing the Dielectric Losses in Heterostructured Ferroelectric Materials

C. Elissalde[1]*, C. Estournes[2], D. Bernard[1], U.C. Chung[1], S. Mornet[1], R. Costes[3], M. Maglione[1], [1]ICMCB-CNRS, Université Bordeaux, Pessac, France; [2]CIRIMAT et Plateforme Nationale CNRS de Frittage Flash, PNF2 MHT, Université Paul Sabatier, Toulouse, France; [3]Thales Research and Technology, Palaiseau Cedex, France

The research and development of electroceramics are driven by the need for miniaturization, cost reduction, and enhanced functionality. An intense research effort was focused in the last decade on heterostructured ferroelectric materials processing. Functional ceramics such as ferroelectric/dielectric composites are promising candidates for electronic applications provided that their dielectric losses are decreased. Dielectric losses can emerge from intrinsic bulk properties and extrinsic contributions (grain boundary, defects, .) affecting the dielectric response in a large frequency range (from kHz to GHz). The performances of ceramics are also determined by the composition, the defects (pores, delamination, charged defects), the second phases (deliberately added, interphases, impurities), and the nature of interfaces. It is a difficult task to control all these parameters while obtaining high densification. The challenge is to find a subtle compromise between the composition, the architecture and the nano/microstructure to tune the dielectric losses in a frequency range as wide as possible. The performance of the ceramics in terms of dielectric losses will be discussed considering the control of interfaces including multi materials assembly using advanced sintering processes.

CH-1:IL08 Thermoplastic Ceramic-polymer Composited of 0-3 Connectivity for High Frequency Applications

H. Jantunen*, J. Juuti, Microelectronics & Materials Physics Laboratory and EMPART Research Group of Infotech Oulu, Oulu, Finland; M.T. Sebastian, National Institute for Interdisciplinary Science & Technology, Trivandrum, India

Composite technology, where a novel artificial material is fabricated by combining ceramic and polymer materials, is earlier widely used for e.g. sonar and medical diagnostics. However, recently several novel ceramic-polymer composites for telecommunication applications have been introduced. Especially thermoplastic composites of 0-3 connectivity, where three dimensionally connected polymer phase is loaded with isolated ceramic particles, are very attractive. These composites enable complex 3D shapes with very inexpensive fabrication methods. Although the process itself is simple needing only proper compounding injection molding systems, choosing the right materials and coupling are very important issues when the best possible structures are designed. Recent investigations have shown that especially using nanotechnology, advanced coating materials or needle or disc shape grains in 0-3 composites, high relative permittivity (εr) and extremely low losses (tanδ = 1/Q) at high frequencies can be achieved. In this review the research carried out within thermoplastic 0-3 ceramic-polymer composites for high frequency applications is gathered together including introduction of same very advance materials and application proposals.

CH-1:IL09 Oxide Nanosheets and Their Integration Technologies for High-k Dielectrics

Minoru Osada*, Takayoshi Sasaki, WPI Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, Tsukuba, Ibaraki, Japan and CREST, JST, Japan

We demonstrate a novel fabrication procedure for high-k dielectrics by using of molecularly-thin oxide nanosheets as a building block. A variety of titano-niobate nanosheets (such as Ti0.87O2, TiNbO5, Ti2NbO7, Nb3O8, and perovsites) were synthesized by delaminating appropriate layered precursors into their molecular single sheets. The elemental nanosheet only consists of TiO6 and NbO6 octahedra, a key building block of oxide dielectrics, which makes the nanosheet as an ideal base for high-k dielectrics with the critical thickness. Layer-by-layer assembly was employed to fabricate high-k dielectric nanofilms of these nanosheets on atomically-flat Pt or SrRuO3 substrates. These nanofilms exhibited both high dielectric constant (100~300) and low leakage current density (<10-7 A/cm2) for thickness down to 5 nm while eliminating problems resulting from the size effect. Our approach provides a rational design and construction of high-k devices.

CH-1:IL10 High Throughput Search of Dielectric Thin Films for Wafer Level Packaging

Ji-Won Choi*, Keun Jung, Seok-Jin Yoon, Wan-Keun Bang, Thin Film Materials Research Center, KIST, Seoul, Korea; Samwon Vacuum Co., Ltd., Gyeonggi-do, Korea

Recently, embedded passive components technology incorporates passive components into an inner layer within multilayer substrates to reduce the size of system level packaging. As one of the embedded passive components, capacitor which is composed of dielectric thin films, has been developed for ultra thin and highly integrated system level packaging. Higher signal transmission speed and embedded densities require dielectric thin films which have various dielectric constant due to increased switching speed and circuit density in thin 3-D module. To develop dielectric compositions to meet these requirements, a continuous composition spread (CCS) method was used to search optimum dielectric properties. Dielectric thin films of binary or ternary compositions were deposited by off-axis reactive co-sputtering using 2 inch target planar magnetron sputter guns arranged at 90o intervals around a three inch-diameter Pt coated substrate (Pt (130 nm)/SiO2 (300 nm)/Si wafer). The capacitance and loss tangent of capacitors were measured at a frequency of 100 kHz and a signal level of 500 mVrms. The composition was inferred as a function of position using Rutherford backscattering spectroscopy along with independent calibration runs.

CH-1:IL11 Thin Films of Advanced Dielectrics for High Frequency Applications: Deposition, (Nano) Characterization and Device Fabrications

Raffaella Lo Nigro, Istituto per la Microelettronica e Microsistemi (IMM)-CNR, Catania, Italy

Microelectronics is driven by an almost insatiable appetite for smaller and faster devices. In memory devices based on capacitive components, such as static and dynamic random access memories, the material permittivity will ultimately decide the degree of miniaturization. In other applications, such as hybrid and Rf circuits, the 95% of chip area consists of capacitors. Their capacitive densities are directly related to the permittivities of the used dielectrics. In this context, dielectric oxides have provided some of the most exciting engineering advances in recent years. Two issues need to be addressed for a complete evaluation of the possible applications of new dielectric oxides in microelectronics devices: the availability of easily scalable deposition techniques and the deep investigation of oxide properties also at the nanoscale. The first issue will addressed through an overview of the Metal-Organic Chemical Deposition route for the fabrication of innovative dielectric oxides thin films. The combination of scanning impedance microscopy and conductive atomic force microscopy will be discussed as valid tool for the characterization, with high lateral resolution at the nanoscale, of inhomogeneous dielectric materials.

CH-1:L12 **Electric Field Breakdown of Polymer Based Nano-composite at Room and Cryogenic Temperatures**

H. Rodrigo[1]*, G.H. Heller[1], A. Ingrole[2], Z (Richard) Liang[2], D.G. Crook[1], S.L. Ranner[1], [1]Center for Advanced Power Systems, Florida State University, Tallahassee, FL, USA; [2]Dept. of Industrial and Manufacturing Engineering, FAMU-FSU College of Engineering, Tallahassee, FL, USA

Electrical breakdown field measurements on Polymethylmethylacrilate (PMMA) and a nano-composite of PMMA + 10% wt of Barium Titanate (BTA) are presented. The measurements were made using uniform field electrode configuration under high voltage DC. The electrodes were made of stainless steel, each having a Bruce profile, and diameter 25 mm. The measurements were made at room temperature (293 K) and liquid Nitrogen temperature (77 K). SEM micrographs are presented, which serve as a diagnostic tool.

CH-1:L13 **High-performance Varactors**

A. Testino, Innovative Task Corporate Material Research & Development, EPCOS OHG, Deutschlandsberg, Austria

Varactors are tunable capacitors. Tuning refers to the ability to change the dielectric permittivity of a material by means of an external stimulus, e.g. a bias voltage. This translates in the field of microwave components as the ability to change the operation frequency by changing the bias voltage. The material properties for a good ceramic varactor are well known: high tunability, low dielectric losses, and low temperature dependence of the dielectric permittivity TCE over the operating temperature range. An optimal trade-off is required among these requirements. An innovative concept and a device manufactured according to this concept are presented in this contribution which overcome some technological limitations of old designs. Concepts, designs and performance of some prototypes will be presented and discussed in details (patent pending).

CH-1:L14 **Influence on the Annealing on the Thermal Stability of Ge-Sb-Te Materials for Recording Devices**

S.A. Kozyukhin*, Kurnakov Institute of General and Inorganic Chemistry, Moscow, Russia; A.A. Sherchenkov, Moscow Institute of Electronic Technology, Russia

Recently we have shown that thermal cycling can lead to the phase separation in Ge-Sb-Te materials and promote reliability issue for the recording devices. In this work we investigated influence of annealing on thermal stability of Ge2Sb2Te5, GeSb2Te4 and GeSb4Te7 synthesized powders by the multiple differential scanning calorimetry (DSC). Annealing was carried out in Ar atmosphere during 105 hours. Multiple DSC scanning lead to the appearance of the unknown endo peak in the temperature range 390-415 C for all compounds. According to the XRD data multiple cycling is accompanied by the phase separation. In this case endo peak can be attributed to the low temperature solid state reactions and melting of eutectic. Increase of the number of DSC scanning is accompanied by the steady increase of the endo peak. However kinetics of the peak is much slower for sintered materials. Higher thermal stability of the annealed powder can be attributed to the slowed diffusion processes. So, annealing of the synthesized powder leads to the sufficient increase of the thermal stability of Ge-Sb-Te materials, which is important for the increased cycling endurance of recording devices.

This work was supported by a grant 08-03-00651 from RFBR.

CH-1:L15 **Low Temperature Electrical and Dielectric Properties of Nb Doped BaSnO3**

Prabhakar Singh[1]*, Om Parkash[2], Devendra Kumar[2], [1]Department of Applied Physics, Institute of Technology, Banaras Hindu University, Varanasi, India; [2]Department of Ceramic Engineering, Institute of Technology, Banaras Hindu University, Varanasi, India

A few compositions of Nb doped $BaSnO_3$ *viz.* $BaSn_{1-x}Nb_xO_3$ (x = 0.001, 0.005, 0.010, 0.050 and 0.100) were prepared by conventional solid state ceramic route. All the compositions were found to be single phase having cubic structure similar to $BaSnO_3$. The electrical and dielectric properties were studied by measuring conductivity and permittivity over temperature range 300 K-125 K and in the frequency range 10^{-2}-10^{6} Hz. Frequency dependence of conductivity was analyzed in terms of Jonscher power law, ($\sigma = \sigma_{DC} + A\nu^{s}$). The variation of exponent factor, s with temperature supports the quantum mechanical tunneling mechanism in the system below 250 K. DC conductivity of the all the compositions was found to follow the Arrhenius behaviour. A change in charge compensation mechanism from electronic to ionic is observed as the composition changed from x = 0.010 to 0.050. Temperature and frequency dependence of dielectric constant, ε' and dissipation factor, tan δ revealed the presence of interfacial and orientational polarizations in these materials.

Session CH-2

Ferroelectrics, Piezoelectrics

CH-2:IL01 **Advances in Pb-free Piezoelectric Materials**

Ahmad Safari, The Glen Howatt Electrocermaic Laboratory, Department of Materials Science and Engineering, Rutgers, the State University of New Jersey, Piscataway, NJ, USA

Environmental and safety concerns with respect to the utilization, recycling, and disposal of Pb-based ferroelectric materials have induced a new surge in developing lead-free ferroelectric materials. (Bi1/2Na1/2)TiO3-based and (K, Na)NbO3-based systems as well as textured domain engineered BaTiO3 ceramics are among the most promising candidates for such lead-free piezoelectric materials. In this talk, the recent advances in processing and electromechanical properties of bulk ceramics, single crystals and thin films are reviewed. The KNN based system is very sensitive to processing conditions such as purity of oxides used and the humidity of the ambient in which processing is accomplished. Despite such sensitivity, the piezoelectric d33 coefficient as high as 350 pC/N can be obtained in randomly oriented KNN-LT-LS ceramics at room temperature. The origin of the high piezoelectric activity will be discussed in the context of polymorphic transitions. The origin of high piezoelectric activity was also investigated by monitoring the temperature dependence of dielectric constant (K) and spontaneous polarization (Ps) in the range -95-200 °C, which will be using in discussing the possible venues for alleviating the strong temperature dependence of piezoelectric properties. The effects of doping such as Ba, Cu and Ag on the electromechanical and acoustic properties will also be discussed and their effects on actuation and acoustic properties will be compared to PZT-4 and PZT-5H. In the BNT based solid solution, the highest piezoelectric properties are at the MPB between rhombohedral and tetragonal phases. The tetragonal side of the MPB with high Td is suitable for actuators and composition in the rhombohedral side with high mechanical quality factor is suitable for high power transducer applications. Direction for Pb-free research is BaTiO3 is very promising. Very high d33 value and high piezoelectric anisotropy (d33/d31) is reported for 98%txtured ceramic with very fine domain size. It has been indicated that the high d33 values are mainly due to extrinsic contributions of 90o domain walls. Also, the most recent development of Pure and doped single phase, <001> oriented epitaxial thin films of (K0.44, Na0.52, Li0.04)(Nb0.84, Ta0.10, Sb0.06)O3 on SrRuO3/SrTiO3 by Pulsed laser deposition will be reviewed. In the pure KNN-LT-LS thin films with submicron thickness, high leakage current was observed which prohibited polarization saturation. Effects of the dopants such as Ba, Mn and Ti on the leakage current have been studied to improve the polarization of the films. Mn-doping of thin films with dominantly c-axis oriented domain structure showed to effectively reduce the leakage and significantly enhances Pr and PS.

CH-2:IL02 **Effect of DC Poling Field on Domain Behaviour in Lead Free Piezoelectric Ceramics**

T. Ogawa*, Department of Electrical and Electronic Engineering, Shizuoka Institute of Science and Technology, Fukuroi, Shizuoka, Japan; M. Furukawa, T. Tsukada, Materials & Process Development Centre, TDK Corporation, Narita, Chiba, Japan

Material research regarding lead free piezoelectric ceramics has been paid much attention because of global environmental considerations. The key practical issue is the difficulty to realized large piezoelectricity such as coupling factors and piezoelectric strain constants. A coupling factor (k) is closely related to the orientation degree of ferroelectric domains through the DC poling process. In this study, the poling characteristics, especially DC poling field (E) dependence of dielectric and piezoelectric properties were investigated to evaluate the domain behaviour in lead free ceramics such as alkali niobate and alkali bismuth titanate ceramics. The domain switching was confirmed by the E to realize minimum dielectric constant (er), minimum k and maximum frequency constant (fc), because of domain clamping. On the other hand, the domain rotation occurred at the E to obtain maximum er and minimum fc. These phenomena are observed in PZT ceramics as well as the lead free ceramics.

This work was partially supported by a Grant-in-Aid for Scientific Research (C) (No. 21560340) from the Ministry of Education, Culture, Sports, Science and Technology, a Research Foundation Grant 2009 jointly sponsored by Academia and Industry of Fukuroi City and the Murata Science Foundation 2009.

CH-2:IL03 Piezoelectric Materials in Thin Form for MEMS and NEMS Applications

D. Remiens, C. Soyer, IEMN-CNRS, Villeneuve d'Ascq, France

Piezoelectric materials are used in many applications as well in bulk as in thin film form. In this later case, the integration with silicon is possible and open a new Integrated Circuit devices applications such as MEMS or NEMS. We present in this talk the performances of some piezoelectric materials: “classical” lead-piezoelectric materials where the PZT is the leader and lead-free piezoelectric material. The films are essantially deposited by rf magnetron sputtering. We show the influence of some fundamentals parameters such as the film orientation, the nature of the top and bottom electrodes on the films properties and in particular on piezoelectric activity and on fatigue. Two piezoelectric materials are presented in details: - PZT and NBT; NBT is a material alternative of PZT: lead free and in bulk form the d33 coefficient is similar to the one of PZT. For integration some technological process have been developed: - Etching at macroscopic scale with IBE and RIE process. The dimension of the micro structure is in the order of 1 to 10 µm. - Etching at nano scale with Ga3+ FIB and nano photolitography. The dimension of the piezoelectric nano structure is in the order of 50 nm. By PFM we have measured good piezoelectric activity on such structures; the size has no effect.

CH-2:IL04 Fractal Geometry and Properties of Doped BaTiO3 Ceramics

V. Mitic[1,2]*, V.B. Pavlovic[3], Lj. Kocic[1], V. Paunovic[1], Lj. Zivkovic[1], [1]University of Nis, Faculty of Electronic Engineering, Nis, Serbia; [2]Institute of Technical Sciences of SASA, Belgrade, Serbia; [3]University of Belgrade, Faculty of Agriculture, Belgrade, Serbia

Taking into account that the complex grain structure is difficult to describe by using traditional analytical methods, in this study, in order to establish ceramic grain shapes of sintered BaTiO3, a new approach on correlation between microstructure and properties of doped BaTiO3 ceramics based on fractal geometry has been developed. BaTiO3 ceramics doped with various dopants (MnCO3, CaZrO3, Er2O3, Yb2O3, Ho2O3) were prepared using conventional solid state procedure, and were sintered at 1350 °C for four hours. The microstructure of sintered specimens was investigated by SEM-5300 and capacitance and dielectric loss measurements have been done using LCR-metra Agilent 4284A. Using the method of fractal modeling a reconstruction of microstructure configurations, like shapes of grains or intergranular contacts has been successfully done. Furthermore, the area of grains surface was calculated using fractal correction that expresses the irregularity of grains surface through fractal dimension. The presented results indicate that the fractal method for analysis of the structure of ceramics provides a new approach for describing, predicting and modeling the grain shape and relations between the BaTiO3 ceramic structure and dielectrical properties.

CH-2:IL05 Theory and Analysis of Transient Response to High Power Signals in Lead-based or Lead-free Piezoelectric Ceramics

T. Tsurumi*, S. Takahashi, M. Hagiwara, M. Yanagihashi, T. Hoshina, H. Takeda, Nano-Phononics Lab., Graduate School of Science and Engrg, Tokyo Institute of Technology, Tokyo, Japan

Piezoelectric devices has been expected as key devices in new electro-mechanic applications, such as inkjet heads, fuel injectors, energy harvesters, various sensors, ultrasonic transducers etc. Piezoelectric actuators and transducers in these applications are mostly driven by high-voltage (or high power) pulse signals. Piezoelectric response to high power signals is mainly determined by the extrinsic effect including domain contributions. The extrinsic effect derives nonlinear response and frequency dependence in electric field induced strain. In this presentation, fundamentals of the domain contribution in the transverse and longitudinal vibrations of PZT-based ceramic resonators are reviewed, and recent results on shear mode vibration are introduced. The theory and analytic method of transient response to high power signals are then explained. The current and vibration velocity of piezoelectric 31-resonators were calculated and fitted to observed data. Incorporation of nonlinear parts as well as loss parts in dielectric and elastic constants was necessary to obtain the best fit. A new precise liquid flow meter using ultrasonic transducers is introduced and results of analytic simulation of the transducer signals are explained.

CH-2:IL06 Integrated ZnO Surface Acoustic Wave Microfluidics and Biosensors

J.K. Luo*, Centre for Material Research & Innovation, University of Bolton, UK; Y.Q. Fu, School of Eng. and Physical Sciences, Heriot Watt University, UK; W.I. Milne, Dept. of Engrg, University of Cambridge, UK

Lab-on-a-chip (LOC) is one of the most important microsystems with promising applications in microanalysis, drug development, diagnosis etc. We have been developing a LOC biodetection system using surface acoustic wave (SAW) as a single actuation mechanism for both microfluidics and biosensing using low cost thin film ZnO piezoelectric material. Acoustic waves coupled into the liquid will induce streaming, or move the droplet if it is on a hydrophobic surface. These can be utilized to make SAW-based micropump and micromixer which are simple in structure and fabrication, are low cost and reliable and effective. SAW devices were fabricated on nanocrystalline ZnO thin films deposited using sputtering and ZnO nanorod films chemically synthesized on Si substrates. A streaming velocity up to ~5cm/s and a droplet pumping speed of ~1cm/s have been achieved. The SAW devices have also been used to detect antibody/antigen biosystem, demonstrated its high sensitivity. It was found that a higher order wave mode, the Sezawa wave is more effective in streaming, transportation of microdroplets and sensing as the transmitted acoustic power is much bigger for Sezawa waves than the Rayleigh waves. The results have demonstrated the feasibility of using a single actuation mechanism for LOC.

CH-2:IL07 MEMS Piezoelectric Energy Harvester with Shear Mode

Seok-Jin Yoon*, Hyun-Cheol Song, Chong-Yun Kang, Thin Film Materials Research Center, Korea Institute of Science & Technology, Seoul, Korea

Energy harvesting from the environment has been of great interest as a standalone power source of wireless sensor nodes for Ubiquitous Sensor Networks (USN). In particular, the piezoelectric energy harvesting from ambient vibration sources has intensively researched because it has a relatively high power density comparing with other energy scavenging methods. Through recent advances in low power consumption RF transmitters and sensors, it is possible to adopt a micro-power energy harvesting system realized by MEMS technology for the system-on-chip. However, the MEMS energy harvesting system has some drawbacks such as a high natural frequency over 300 Hz and a small power generation due to a small dimension. To overcome these limitations, we devised a novel power generator with a spiral spring structure. The natural frequency of a cantilever could be decreased to the usable frequency region (under 300 Hz) because the natural frequency depends on the length of cantilever. The MEMS cantilever with the spiral spring structure was fabricated by a silicon MEMS process. In this study, the natural frequency of the energy harvester was a lower than a normal cantilever structure and sufficiently controllable in 50 - 200 Hz frequency region as adjusting weight of a proof mass. Moreover, the MEMS energy harvester had a higher energy conversion efficient because a shear mode (d_{15}) is much larger than a 33 mode (d_{33}) and the energy conversion efficiency is proportional to the piezoelectric constant (d). We expect the spiral type MEMS power generator would be a good candidate as a standalone power generator for USN.

CH-2:L09 Linear Characterization at Shear Resonance of Lossy Piezoceramics Using a Non-standard, Thickness Poled, Shear Plate

L. Pardo[1]*, F. Montero de Espinosa[2], A. García[1], K. Brebøl[3], [1]Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Cantoblanco, Madrid, Spain; [2]Instituto de Acústica, CETEF, CSIC, Serrano, Madrid, Spain; [3]Limiel ApS, Langebæk, Denmark

When a resonator is used to determine the complex material properties from complex impedance measurements at its electromechanical resonance, not only the accurate determination of the characteristic frequencies is needed. Instead, accurate values of impedance around resonance and antirresonance frequencies are also required to properly determine the material losses. Thus, uncoupled resonances are desired. The, thickness poled, shear plates used for the material characterization present mode coupling of the pure shear mode and other plate modes, like contour modes. The authors recently studied how to obtain a shear resonance with minimum coupling to other disturbing modes[1]. Examples of this process will be presented for commercial PZT and lead-free ceramics under development. An study of the evolution of the complex material parameters with the change in the aspect ratio of this thickness poled shear plate is here presented. These are obtained by Alemany *et* *al* software[2]. A Navy II type commercial PZT ceramic was used in this study and samples amenable for material characterization obtained in a wide range of aspect ratios below 15:1. The reliability of the material properties obtained is tested with the use of Finite Element modeling of this non-Standard, thickness poled, shear plate resonator.

[1]Pardo L., Montero de Espinosa F., García A. and Brebøl K., Applied Physics Letters (2008); [2]Pardo L., Algueró M. and Brebøl K., Journal of Physics. D: Applied Physics. 40 2162 (2007).

CH-2:IL10 Large Remanent Polarization in BiFeO3 Based Single Crystals

Yuji Noguchi*, Hiroki Matsuo, Yuki Kitanaka, Masaru Miyayama, Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo, Japan

Bismuth ferrite (BiFeO3) has attracted a great deal of attention as a promising multiferroic material showing both ferroelectric and (anti)ferromagnetic properties at room temperature. Although Ps of BiFeO3 thin films can be switched by applying an electric field, a huge coercive field (Ec) constitutes an obstacle in the way of the FRAM and multiferroic applications. In this paper, it is demonstrated that the novel materials design based on defect control, defect-induced polarization switching, is effective for decreasing Ec for BiFeO3 single crystals. First, we performed first-principles calculations based on density functional theory within generalized spin-density gradient approximation using PAW potentials method (code VASP). Experiments show that Ti4+ and Ni2+ are difficult to be substituted at the Fe site. Therefore, a set of Zn2+ and Mn4+ was selected for defect-induced polarization switching in BiFeO3. Although undoped crystals did not exhibit a ferroelectric polarization at all, the crystals doped with Zn2+ and Mn4+ showed a well-saturated polarization hysteresis loop with a remanent polarization of 37 mircoC/cm2 and an Ec of 20 kV/cm.

CH-2:IL11 Piezo-ferroelectric Thin Films: From Nucleation to Functionality

P. Muralt, Ceramics Laboratory, Swiss Federal Institute of Technology EPFL, Lausanne, Switzerland

The field of piezoelectric thin film microsystems combines an exciting richness of potential applications with many attractive scientific topics on materials processing and physical properties. This talk will strive to address this broad area from process to performance. Strong ferroelectricity is a pure effect of the crystalline lattice. Thus, crystalline quality of the material plays a crucial role. For real applications, one cannot compromise on materials performance. Integration tasks must be well accomplished to obtain a dense, phase pure material with controlled texture, and a suitable film thickness. PZT is still the most advanced material for ferroelectric thin films. Remains the question whether further improvements are still possible. There are indeed no simple data and theories available that would instruct us where the limit is, as in the case of non-ferroelectric piezoelectrics for which the knowledge of single crystal properties gives all the answers. Reasons for this complication are domain contributions in combination with the clamping to elastic structures, and deviations from ideal microstructure and interfaces. For full assessment, nano-scale as well as micro-scale properties are of importance. After the view on nano and microscopic phenomena, results on various applications will be shortly presented, such for energy harvesting, ultrasonic transducers, and microphones. The current state of the art in processing, properties and applications is addressed, and an outlook for further improvements is given.

CH-2:IL12 Correlation Between Powder Properties and Processing Conditions of Mechanically Activated Nanocrystalline BaTiO3

V.B. Pavlovic*, Faculty of Mechanical Engineering, University of Belgrade, Belgrade, Serbia; V.P. Pavlovic, Joint Laboratory for Advanced Materials of the Serbian Academy of Sciences and Arts, Belgrade, Serbia; J. Krstic, Institute of Chemistry, Technology and Metallurgy, Dept. of Catalysis and Chemical Engineering, Belgrade, Serbia; M.J. Scepanovic, Center for Solid State Physics and New Materials, Institute of Physics, Belgrade, Serbia; V. Mitic, Fac. of Electronic Engineering, University of Nis, Serbia; J. Blanuša, Vinca Institute of Nuclear Sciences, Belgrade, Serbia; D. Popovic, Faculty of Physics, University of Belgrade, Serbia

Increasing demands on the quality of electronic ceramics requires a well-controlled correlation between particle morphology and processing conditions. Taking into accont that the production of nanoparticles by mechanical activation does not only depend on particles comminution, but also on the capability of stabilization of broken fragments and their rheology, in this article structural investigations of mechanically activated $BaTiO_3$ powders have been presented. The investigations of specific pores volume, porosity and microstructure morphology, have been performed using mercury porosimetry analysis and scanning electron microscopy. The lattice vibration spectra of non activated and activated samples, their phase composition, lattice microstrains and the mean size of coherently diffracting domains were examined by Raman spectroscopy and X-ray powder diffraction. The change of the IR active modes was investigated by IR measurements. Semi-quantitative comparison of the $BaCO_3$ and OH^- group presence in IR spectra was calculated.The presented results enable establishing processing parameters that are indisensable for obtaining materials with advanced properties.

CH-2:L13 Preparation of Textured Niobium-doped Bismuth Titanate Ceramics by Tape Casting

E.C. Aguiar, E. Longo, J.A. Varela*, Chemistry Institute, UNESP, Araraquara, SP, Brazil

Bismuth layer structured ferroelectric (BLSF) ceramics are a major candidate in lead-free materials for piezoelectric devices such as filters or oscillators, capacitors and memories due to their high Curie temperature and excellent heat resistance. Pure and niobium doped Bi4Ti3-xNbxO12 (x = 0, 0.1, 0.2, 0.4) textured ferroelectric ceramics were prepared via Template Tape Casting Method. The starting powders were obtained from the polymeric precursor method at low temperature and template particles were produced from molten-salt method. Aqueous solvent was used to obtain the viscous slurries containing initial powders, dispersant, binder, plasticizer and 5 wt.% template particles. Thick films were deposited at room temperature in a Tape Cast using a 120 µm opened doctor blade. After drying thicks were stacked, pressed, cut, calcined at 500oC for 3h and sintered at 800oC for 1h. C-axis oriented ceramics were characterized by X-ray diffraction (XRD), scanning electronic microscopy (SEM), relative density (Archimedes method) and conductivity. Results indicated highly c-axis-oriented Bi4Ti3O12 thick films in a perpendicular direction of the tape cast deposition, with 95% of theoretical density. Moreover, the conductivity of the niobium-doped compositions is decreased due to p-type semiconducting behavior.

CH-2:L15 Electromechanical Properties of BaTiO3 Ceramics Prepared by Spark Plasma Sintering

Hiroshi Maiwa*, Naoki Matsumoto, Shonan Institute of Technology, Fujisawa, Japan

The recent demands for lead-free piezoelectric materials recall the barium titanate (BaTiO3, BT) applied in limited areas, such as sonar. BaTiO3 (BT) ceramics with various grain sizes are prepared by spark plasma sintering (SPS), two-step sintering, and conventional sintering. The relative densities of the BT ceramics prepared by SPS at 950 °C and postannealed at 1000-1200 °C are 5.95-6.00 g/cm3. The field-induced displacement and piezoelectric constant measured by a resonant-antiresonant frequency method are evaluated. The BT ceramics prepared by SPS are characterized by high permittivity exceeding 5000, linear-field-induced strain, low Qm, and exhibit a relatively higher field-induced strain exceeding X33 = 500pm/V and a higher d31 value than the fine-grained BT ceramics fabricated by other methods. These characteristics of the SPS-BT ceramics are probably due to the high internal stress of the samples.

CH-2:L17 Impedance Modelling of Multi-layer Ceramic Capacitors

Jong-Sook Lee*, Yong Kim, Eui-Chol Shin, Hyun-Ho Seo, Chonnam National University, Gwangju, Korea; Ji-Young Park, Chang-Hoon Kim, Gang-Hun Hur, Samsung Electromechanics, Korea

Impedance measurements have been performed on different classes of multilayer ceramic capacitors such as X5R, X7R, Y5V and C0G over a wide temperature and frequency range. Characteristic dependence of each MLCC type on frequency, temperature, and AC level was observed, which is to be explained in terms of the dielectric and conductive property of the ceramic bulk and of the interfaces such as grain boundaries and ceramic/metal electrode boundaries. Based on the understanding of the physical processes robust equivalent circuits for different MLCC types will be proposed.

CH-2:L18 Stress Induced Effect on Electrical Properties of CSD-derived Ferroelectric Thin Films

Hisao Suzuki[1], Tomoya Ohno[2], Naonori Sakamoto[1], Naoki Wakiya[1], Takeshi Matsuda[2], Takashi Hayashi[3], [1]Shizuoka University, Hamamatsu, Shizuoka, Japan; [2]Kitami Institute of Technology, Japan; [3]Shonan Institute of Technology, Japan

The electrical properties of the ferroelectric thin films are affected by many factors such as composition, orientation, and residual stress in films. Especially, the residual stress in ferroelectric thin films should have great effect on the electrical properties of the resulting ferroelectric thin films. However in the case of ferroelectric thin films on a commercially used Si wafer, the residual stress in films is usually tensile because of the low thermal expansion coefficient of a Si, leading to the reduced electrical properties. Therefore in this study, oxide electrode thin film with a controlled nanostructure was deposited on a Si wafer to control the residual stress in thin films. The porous nanostructure of a lanthanum nickel oxide with a preferred orientation and high thermal expansion coefficient acted as a buffer layer to relax the tensile stress from a Si substrate and constraint layer to apply the compressive stress to the ferroelectric thin film. The high compressive stress resulted in the enhanced electrical properties of the ferroelectric thin films such as excellent ferroelectricity, giant piezoelectricity and MPB shift for the CSD-derived PZT thin films. These results indicated the importance of the stress engineering for the ferroelectric thin films.

CH-2:L19 Synergistic Information Encoding by Combinatorial Pulse Operation of Ferroelectric Ceramic Capacitors

D. Ricinschi*, T. Kanashima, M. Okuyama, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

In this work we explore beyond binary memory capability of ferroelectrics, aiming to render them able to encode multiple bit information, based on operation in a regime spanning several polarization reversal mechanisms. Accessing a Pb(Zr,Ti)O3 (PZT) ceramic capacitor with combinatorial sequences of two pulses whose amplitude, width and polarity are all allowed to vary during polarization reversal, eight partially-switched multiple-level memory states are reproducibly generated. The signature of any of the two applied pulses is discernable irrespective on not only its own polarity and the other's polarity, but also on their succession. Consequently, while the ferroelectric in the saturated polarization regime would encode a single information bit, reading a partially switched state created by the combinatorial pulses determines the value of 3 bits simultaneously. More generally, we imply that appending to the operation protocol a comparative examination of ferroelectric's reaction allows multiple-bit information to be encoded. Formulating this as a "material-operation synergy encoding" principle, we demonstrate, with aid of applied mathematics, that a single PZT capacitor is rendered able to encode and store up to 64 bits of data.

CH-2:L21 Preparation and Properties of Lead Free Alkali Niobates Doped with Bi and Cu

C. Miclea*, C. Tanasoiu, C.F. Miclea, L. Amarande, L. Trupina, M. Cioangher, National Institute for Materials Physics, Magurele-Bucharest, Romania; C. Plavitu, C.T. Miclea, M. Susu, Hyperion University, Bucharest, Romania

Lead containing PZT tzpe materials have dominated the world market for piezoelectric materials due to their high performance in all fields of application as sensors and transducers. Their major drawbacks consist in the high amount of lead oxide they contain which proved to be toxic for organisms. Therefore, there is a great concern to find alternatives to such materials with lead fee ones. Solid solutions of kalium and sodium niobates proved to be the best choice. In the present work we have prepared dense lead free ceramics of KNN doped with Bi and Cu with compositions corresponding to the formula (1-x)KNN.x(Bi2O3,CuO) with 0.0=x=0.1. The materials were synthesized by the usual solid state reaction. We studied the effect of Bi and Cu on the sinterability and piezoelectric properties of the sintered ceramics. Densities of 4.68 g/cm3 were obtained for samples sintered at 1150 °C for 6 hours. A typical morphotropic phase boundary was detected for composition around x=0.06 where the piezoelectric parameter showed maximum values. Thus the planar coupling factor kp was 0.46, the piezoelectric charge constant d33 was 270 pC/N and the mechanical quality factor Qm was 75. Such composition can be successfully used as sensors for different transducers.

Session CH-3
Magnetic Ceramics

CH-3:IL01 Magnetostrictive Galfenol Torque Sensor Devices for Smart by-Wire Steering System in Automobile Technology

Yasubumi Furuya*, Teiko Okazaki, Science and Technology, Hirosaki University, Hirosaki, Japan; Chihiro Saito, Namiki Precision Company, Japan; Muneaki Shimada, Nissan Motors, Japan

Polycrystalline Galfenol (Fe-Ga-X, X=Al, C, Zr etc.) alloys were fabricated as a bulk sample from rapid-solidified powders or ark-melted and annealing process method for enhancing various engineering applicability. (Fe-Ga0.15-Al0.05)99.0-Zr0.5-C0.5 [at.%] sample showed a maximum magnetostriction of λmax=90ppm to 150ppm as well as a tensile stress over σ=800MPa. This large magnetostriction is mainly caused by non-precipitating of the ordered A2 phases without the excessive precipitation of ordered phases such as fcc ordered L12 and bcc ordered D03 phases and the remained [100] oriented strong textures by a heat treatment. Based on the improvements of these properties in the developed bulk Galfenol alloys FeGaAlX. Secondarily, we will introduce an application as a smart torque sensor by utilizing Galfenol-ring around the steering shaft for steering-by-wire system of automobile. In this system, a torque sensing system by using the magnetostrictive ring of FeGa (Galfenol) alloy was developed and magnetic flux leakage from the Galfenol ring attached on the rotating shaft was experimentally measured by using two differential Hall probe sensor. A promising result on ring-type inverse magnetostrictive torque sensor will be presented.

CH-3:IL02 Magnetic Oxide Thin Films Grown by Pulsed Laser Deposition for Applications in Spintronics

L. Morellon[1,2,3]*, J.Orna[1,3], G. Simon[1,3], P.A. Algarabel[2,3], J.A. Pardo[1,4], A. Fernandez-Pacheco[1,3], C. Magen[3,5], J.M. De Teresa[2,3], M.R. Ibarra[1,2,3], [1]Instituto de Nanociencia de Aragon, Universidad de Zaragoza, Zaragoza, Spain; [2]Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza-CSIC, Zaragoza, Spain; [3]Departamento de Física de la Materia Condensada, Universidad de Zaragoza, Zaragoza, Spain; [4]Departamento de Ciencia y Tecnologia de Materiales y Fluidos, Universidad de Zaragoza, Zaragoza, Spain; [5]Instituto de Nanociencia de Aragon-ARAID, Universidad de Zaragoza, Zaragoza, Spain

Half-metallic compounds present a great potential for room-temperature applications in Spintronics. Among those, much work has been devoted to magnetite, Fe3O4, and other more complex oxides such as the double perovskites, e.g. Sr2CrReO6 (SCRO). In this contribution, our recent efforts to grow high-quality epitaxial thin films of both Fe3O4 and SCRO by Pulsed Laser Deposition will be reviewed. This will be demonstrated by an extensive experimental characterization including x-ray diffraction and x-ray reflectivity, high-resolution transmission electron microscopy, atomic force microscopy, Polarized Neutron Reflectivity, and VSM and SQUID magnetometry. The study of the magnetotransport properties such as the Hall Effect is one of our main interests. We report a systematic study of the anomalous Hall effect, planar Hall effect, and ordinary Hall effect in epitaxial Fe3O4 thin films grown on MgO (001) within a wide range of thicknesses (5 - 150 nm) and in the temperature range from 300 K down to 60 K. Recent interest of these materials for thermoelectric conversion in half-metals based on the spin Seebeck effect will be also proposed and demonstrated. In addition, we will also present our efforts to produce epitaxial heterostructures based on these materials.

CH-3:L04 Oriented Barium Hexaferrite Thick Films Prepared by Electrophoretic Deposition in a Magnetic Field

Simona Ovtar*, Darja Lisjak, Miha Drofenik, Jozef Stefan Institute, Ljubljana, Slovenia

Charged particles in a suspension can be deposited by electrophoretic deposition (EPD) on a conductive substrate to produce homogeneous deposits and films. Hard-magnetic barium hexaferrite (BaHF) particles have a high intrinsic magnetocrystalline anisotropy and tend to orient in a magnetic field. Therefore, the orientation of the particles in deposits/films can be controlled with an external magnetic field. These oriented deposits of BaHF have great potential for use in future microwave and millimetre-wave devices. BaHF suspensions made from powders with particles sizes from 8 to 300 nm were prepared with the adsorption of a surfactant called dodecylbenzene sulfonic acid onto the particles' surfaces. The latter were studied with zeta-potential measurements and IR spectroscopy. The stable suspensions were subsequently used for the preparation of films by EPD. Different EPD-cell designs were studied and deposits with different degrees of orientation were prepared. An additional improvement in the orientation, up to 92%, of the deposits was obtained when the magnetic field was applied during the EPD. After that the deposits were sintered to produce magnetic films, the orientations of which were determined from the magnetic hysteresis loops in combination with XRD analyses.

CH-3:IL05 Beyond Conventional Magneto-optical Spectroscopy of Magnetic Oxides

J.M. Caicedo, G. Herranz*, D. Hrabovský, F. Sánchez, I.C. Infante, J. Fontcuberta, Institut de Ciencia de Materials de Barcelona (ICMAB), CSIC, Campus de la UAB, Bellaterra, Catalonia, Spain; R. Ramos, S.

K. Arora, I.V. Shvets, Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), School of Physics, Trinity College Dublin, Ireland

Magnetooptics (MO) comes from the interaction of light with magnetized matter. First-order MO effects are revealed as a rotation and ellipticity of the light polarization or changes of the reflectivity proportional to the magnetization. While this is usually exploited to investigate the magnetic properties of materials here we show that higher-order MO effects can also develop concomitantly with linear MO effects near the metal-insulator transitions of many magnetic oxides. The origin of this non-linear response is diverse, depending on whether it arises from a quadratic MO response or it is originated by magnetorefractive effects. We have analyzed the dependence of these higher-order contributions as a function of temperature and electromagnetic wavelength, as well as on external stimuli such as strain and electric fields in different oxides, including magnetite and manganites of different chemical composition. By inspecting the MO signal near the transition in the visible and near-ultraviolet part of the spectrum, we probe electronic transitions of the order of the eV providing thus an invaluable tool to gain insights into the nature of the structural and electronic transitions driven by magnetic/ electric fields or by temperature in these strongly electron correlated systems.

CH-3:IL06 Spin and Orbital Magnetic Moments in Magnetic Double Perovskites Probed by X-ray Magnetic Circular Dichroism Under High Magnetic Fields

M. Sikora, PACS, AGH University of Science and Technology, Krakow, Poland

Magnetoresistive double perovskites, A2FeReO6, with Tc above room temperature have recently attracted great attention not only due to possible technological application but also due to uniqe magnetic properties - high coercivity and field induced phase transitions. They are attributed to the strong magnetostructural coupling via not fully quenched orbital moment of Re. We present a study of spin and orbital contributions to the magnetic moment of Rhenium employing X-ray Magnetic Circular Dichroism technique in a wide temperature (10-250K) and magnetic field (up to 30T) range. Measurements revealed a substantial Re orbital moment, ~30% of that of spin moment, which varies across the structural phase transition reported in Ca2FeReO6 compound. A comparison of the field and temperature dependences of the rhenium XMCD and bulk magnetization shows that the Re sublattice is magnetically softer and more sensitive to the temperature and field change at $T < 150$ K. The results are explained within a scenario of field induced phase coexistence and transition between two monoclinic phases of diverse magnetocrystalline coupling, which plausibly explains the colossal magnetoresistance observed in the compound studied.

CH-3:L07 Magnetoelectric Coupling in Multi-ferro Fe-Pd / PZT / Fe-Pd Laminate Composites

Teiko Okazaki*, Yasubumi Furuya, Yusuke Sado, Science and Technology, Hirosaki University, Hirosaki, Japan; Chihiro Saito, Namiki Precision Company, Japan

Ferromagnetic /ferroelectric composites are drawing attention since they exhibit classes of physical properties with magnetoelectric (ME) response significantly larger than those of single phase materials. The magnetoelectric effect can be used in various applications such as microwave field and current measurement. Also, a magnetoelectric sensor will be an alternative tool of the Hall sensor for magnetic field measurement. We investigated ME effect in ferromagnetic shape memory alloy Fe-Pd films sputtered on both surfaces of Pb(Zr, Ti)O3 (PZT) laminate composites, to be applicable for small magnetic field sensor. Ferromagnetic shape memory Fe-Pd alloy exhibits magnetic field induced strain of 1000 ppm, which compares with large magnetostriction of Terfenol-D. Electric voltage generated when the composites are subjected to a magnetic field increased with thickness of sputtered Fe-Pd film. Magnetoelectric voltage coefficient dE/dH in Fe-Pd(10 µm) / PZT(260µm) / Fe-Pd(10 µm) laminate composite is 4.5 V/cm.Oe, which nealy equal to a large value of 4.68 V/cm.Oe obtained in Terfenol-D / PMN-Pt laminate composites.

CH-3:IL10 Novel Materials for all Oxide-based Spintronics

L. Alff, Institute for Materials Science, TU Darmstadt, Darmstadt, Germany

It is a challenge of materials science to find suited materials for applications in spintronics. Within the fascinating class of perovskites the ferrimagnetic double perovskites combine high Curie-temperatures with a half-metallic nature of the charge carriers[1]. Besides the structural, magnetic, and transport properties, particular focus is on possible strategies to taylor the physical properties of ferrimagnetic double perovskites in order to achieve still higher Curie-temperatures, tunable spin-polarized conductivity[2], and to understand the origin of the observed high Curie-temperatures[3]. Even more, completely new properties as antiferromagnetic half-metallicity and multiferroicity is envisaged. Possible applications of the ferromagnetic double perovskites are discussed within an all oxide nano-electronics, as for example an all oxide tunneling magnetoresistance (TMR) device.

[1] L. Alff, in Electron Correlation in New Materials and Nanosystems, K. Scharnberg and S. Kruchinin eds., NATO Science Series II: Mathematics, Physics and Chemistry 241 (2007); [2] Y. Krockenberger et al, Phys. Rev. B 75, 020404(R) (2007); [3] A. Winkler et al., New J. Phys. 11, 073047 (2009)

CH-3:IL11 Magnetic Nanoparticles for Applications in Medicine and Technique

P. Goernert*, P. Payer, M. Roeder, Innovent, Jena, Germany; R. Mueller, R. Hergt, IPHT, Jena, Germany; H. Stepankova, P. Kristan, V. Chlan, Charles University, Prague, Czech Republic

A brief overview is given on magnetic nanoparticles (NP) prepared by wet-chemical and gas-phase synthesis as well as glass crystallization. Such magnetic NP are used for experimental and commercial applications in medicine and technique. Here we focus the attention on magnetic iron oxide NP with diameters between 5 and 150 nm prepared wet-chemically and by glass crystallization. Characterization is carried out by electron microscopy, X-ray diffractometry, photon correlation spectroscopy (PCS), SQUID and vibrating sample magnetometry, nuclear magnetic resonance (NMR), magnetic and magnetooptical relaxation. The maximum diameter of magnetic single domains of magnetite has to be estimated in the order of 80 nm. Carboxymethyl dextran (CMD) coated magnetic iron oxides are applied for magnetic separation of tumour cells as a function of time and medium. The absorption of electromagnetic waves is used in medicine for tumour therapy (hyperthermia) and for technical applications for gluing of materials and shielding of electromagnetic waves. Another application of magnetic nanoparticles is reduction of sedimentation of magnetorheological fluids e.g. for hydraulic shock absorbers.

CH-3:IL12 Application of Permanent Magnets for Microwave Absorbers in GHz Range

Satoshi Sugimoto, Department of Material Science, Graduate School of Engineering, Tohoku University, Sendai, Japan

Recently, the number of communication devices using GHz-range microwave radiation has been increased and much attention has been paid to microwave absorbers. The authors have reported that hard magnetic materials such as M-type ferrite, R2Fe14B (R: rare earth) and Sm2Fe17 compounds, can be used as microwave absorbers at these high frequencies. To control the functional frequency range, the natural resonance frequencies (fr) of these hard magnetic materials have to be shifted and substitutions of elements are effective method for the shift. The resin composite of BaFe9(Ti0.5Mn0.5)3O19 exhibited the good microwave absorption at frequencies of 12-20 GHz with wide bandwidth. The (Nd0.725Sm0.275)2Fe14B and (Y0.9Sm0.1)2Fe14B also showed good microwave absorption properties at 60 GHz and 22 GHz, respectively. The use of an exchange interaction with a soft magnetic phase like the case of nanocomposite magnets is another method for the fr shift. The Y9.4Fe79.3B11.1Cu0.2 resin composite exhibited good microwave absorption properties (over 99%) at 39.5 GHz. On the other hand, the disproportionation reaction of the Sm2Fe17 compound by nitrogen produced two-phase nanostructure composed of Fe and Sm nitride. The resin composites exhibited microwave absorption in the several GHz range.

Session CH-4

Varistors and Thermistors

CH-4:IL01 Low Temperature Deposition of Nickel Manganite Thin Films

Song Won Ko*, Jing Li, Elizabeth Dickey, Susan Trolier-McKinstry Materials Research Institute, Pennsylvania State University, University Park, PA, USA

Ceramic thermistors like VOx, a-Si, and NiMn2O4 are used for thermal sensing applications such as microbolometers and infrared sensors.

These materials should have high negative temperature coefficient of resistance, high sensitivity, and low noise for these applications. Nickel manganite films have large TCR (>-3%/K) and good environmental stability, so that the properties are robust during subsequent processing. To improve the ability to prepare manganite spinels on pre-existing circuitry, new techniques that enable low temperature depositions need to be developed. To address this, the spin spray technique was adopted in this work; this approach is both low cost and permits low process temperatures(<100 °C). Spin spray deposition is accomplished using two dilute water-based solutions. To grow films the solution was nebulized by a nitrogen carrier gas and sprayed onto a rotating SiO2/Si substrate. As deposited nickel manganite films were nanocrystalline spinel by TEM analysis. The temperature coefficient of resistance was around -3.6%/K and activation energy was about 0.36eV. The doping of Zn increased crystallinity of as-deposited nickel manganite films but resistivity increased as well. In contrast, Cu doping allowed the electric resistivity to be tuned to less than 1000 Ω-cm.

CH-4:IL02 **Energetics and Electronic Structure of Native Defects and Dopants in ZnO**

F. Oba, Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto, Japan

The technological importance of ZnO has stimulated a fair amount of research on its native defects and dopants in previous decades. However, fundamental issues such as the source of the n-type conductivity and the strategy for the p-type doping remain controversial. First-principles studies have also addressed these issues, but the yet reported results include uncertainties due to the insufficient description of the electronic structure and the slow convergence with the simulation cell size. In this talk, I will discuss the energetics and electronic structure of point defects in ZnO on the basis of hybrid density functional calculations combined with cell-size corrections. This approach overcomes the aforementioned drawbacks and provides a clear picture of the defects: i) the O vacancy and H impurity, which are deep and shallow donors, respectively, can form with a substantial concentration in n-type ZnO; ii) the Zn interstitial is a shallow donor but has a high formation energy; and iii) the O vacancy contributes to nonstoichiometry and H acts as a donor under O-poor conditions, both of which are without significant compensation by the acceptor-like Zn vacancy. These results will be discussed comparatively with related reports including those on n- and p-type doping.

CH-4:IL03 **Preparing and Electric Properties of BaTiO3-based Lead-free PTCR Ceramics**

G.R. Li*, S.L. Leng, L.Y. Zheng, J.T. Zeng, H.R. Zeng, T.B. Wang, Q.R. Yin, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China

Curie temperature (Tc) of BaTiO3 (BT) is about 130 °C, which limits the applications of BT-based PTCR. PbTiO3 (Tc = 490 °C) is usually used to form solid solutions with BT to increase the Tc. Commercial BT-based PTCR ceramics with high Tc contain Pb. In this report, lead free PTCR ceramics, BT-BNT, BT-BKT, and BT-BNT-BKT solid solutions, were prepared by the conventional solid reaction method. Donors doping such as Y2O5 and Nb2O5, additive modification of MnO2, and also co-doping of donor and acceptor in grain and grain boundary, are investigated to obtain high PTCR effect. The inhibition of grain growth by CaO, and glass additives of Al2O3-SiO2-BaO are investigated to improve the ceramics density, electric microstructure, and electric properties under high applied fields. Multi-stage soaking and fast heating procedure in sintering process are tried to understand the mechanism of PTC effect for these lead free systems. Low room-temperature resistivity (ρ25) of 30 - 80 Ω.cm, and a high resistivity jump (ρmax/ρmin) of 4.2 orders of magnitude of BT-based lead free PTCR with Tc about 152 °C are obtained, and the distinct PTC effect with Tc between 185 and 232 °C are also prepared by sintering in N2. The XRD patterns, SEM, TEM methods are used to investigate the microstructure of PTCR ceramics. Temperature dependence of electric properties for grain and grain boundary are investigated by impedance analysis. The results show that BT-based lead free PTCR can reach high PTC effect to satisfy the high temperature applications by suitable donor doping and processing conditions.

CH-4:IL04 **Defect Structure of Zinc Oxide and Related Properties**

Hajime Haneda[1]*, Isao Sakaguchi[1], Naoki Ohashi[1], Haruki Ryoken[1, 2], Shunichi Hishita[1], [1]National Institute for Materials Science, Tsukuba, Ibaraki, Japan; [2]Department of Applied Science for Electronics & Materials, Kyushu University, Kasuga, Fukuoka, Japan

Compounds with wurtzite crystal structure such as GaN, AlN, ZnO and so on are very useful for practical applications, which are the light emitter device, SAW device, varistor, etc. Lots of characteristics are generally governed by roles of lattice defects. Hence, illuminating roles of these lattice defects is essential for understanding and controlling the characteristics of devices. In the present report, we are summarizing these diffusivities in the compounds with the wurtzite structure, i.e. ZnO, AlN, GaN, and discussing the diffusion mechanism and the defect structure in these materials. The isotopic heterostructural thin films were successfully obtained in systems of $Zn^{16}O$-$Zn^{18}O$, ^{64}ZnO-^{68}ZnO, $Ga^{14}N$-$Ga^{15}N$ and $Al^{14}N$-$Al^{15}N$, using PLD and MBE thin film deposition methods. These ions diffusions are mediated by the vacancy. The nitrogen ion diffusivities were also measured in GaN and AlN thin films. The nitrogen diffusivity in GaN was lower than the reported values. We will discuss the relation between these properties and defect structure.

CH-4:IL05 **Local Measurements of Functional Properties in Electro-ceramics**

Colin Leach, School of Materials, University of Manchester, Manchester, UK

The homogeneity of an electroceramic may be characterised in terms of the minimum length scale over which identical electrical measurements can be made. Deviations from average behaviour can take the form of fluctuations about a mean value, or systematic variations due to an underlying microstructural or microchemical gradient. As the size of electroceramic components continues to reduce, ever smaller scale variations in a material's performance become significant, both from device performance and batch consistency perspectives. It has long been realised that variations in the physical microstructure provide only limited insight into the homogeneity of electrical performance of a device. Consequently, methods have been developed to observe directly the "electrical microstructure" of a ceramic, through a combination of localised property measurement and the characterisation of individual, internal, structures responsible for functional behaviour. Many studies of localised electrical property measurements have been made using surface mounted electrodes, frequently across single grain boundaries in polycrystalline or bicrystal electroceramic samples, enabling resistance, impedance, and so on, to be characterised. Data collected in this way generally produces a spread of measured values, with an average close to the bulk measured property but is dependent on the length scale of measurement and the homogeneity of the sample. Our approach is to take into account the effect of adjacent structures, by using variable electrode spacings that span several grains to record "local average" values. Direct observation of electrical barrier structures, responsible for functional behaviour can be made using conductive mode (CM) microscopy, which uses currents flowing in the specimen under beam irradiation as the image-forming signal. Depending on how the current is collected, various signals are available, including: specimen current, β-conductivity, resistive contrast and electron beam induced current (EBIC). Each of these signals gives information about a different aspect of the electrical structure, and can be used individually or in combination, along with quantitative modelling and simulation techniques to establish material parameters from the experimental data. In this presentation the role of local property and electrical structure measurements, collected over various length scales, in the development of functional electroceramics will be reviewed, and illustrated with examples taken from our recent work in the areas of varistors, PTC thermistors and piezoelectric materials.

CH-4:IL06 **Advances in Varistor Ceramics**

F. Greuter, ABB Corporate Research, Baden-Daettwil, Switzerland

Metal oxide varistors based on doped ZnO are today the established key elements for overvoltage protection, starting at ~3V for electronics and extending up to >1 MV for UHV power grids. Over the last 40 years since the discovery of the ZnO-varistor, much progress has been made on all relevant aspects of the technology: from basic understanding of the varistor effect to new products like multilayer elements, microvaristors or high field materials and to the many challenges from the economic manufacturing of the semiconducting ceramics on a large scale. A consistent model describing the highly nonlinear response of single grain boundaries, extensive microscopy work and some modeling of the nanoscale grain boundary films provide today a detailed insight of the varistor effect. Improved control of the microstructure is essential for exploiting these materials to their electrical, mechanical and thermal limits and raising their energy absorption capability. This requires the continuous implementation of advances in ceramic process technology and a deeper understanding of the failure mechanisms. An overview will be given on the current understanding of the electrical and materials aspects of varistors, the requirements in industrial applications and some recent new developments.

CH-4:IL07 Origin of Stoichiometry Influence in High Performance NaxCo2O4-y

Sean Li, School of Materials Science and Engineering, The University of New South Wales, Sydney, Australia

Materials of NaxCo2O4-y with various atomic stoichiometric ratios were prepared carefully with solid state reaction method. The crystallographic information obtained from high resolution neutron diffraction provides experimental data for ab initio calculation to identify the actual atomic occupancies in the lattice structures and investigate the effect of composition on phonon behaviours. The thermal and electrical properties of the as-prepared materials were characterized with high temperature Seeback Probe, Laser Flash and Hall Effect measurement systems etc. The underlying fundamental mechanism of composition-dependent thermal performance of NaxCo2O4-y has been unfolded by the calculated and experimental results, providing an insight into the optimization of the materials for vital applications.

CH-4:IL08 NTC Thermistors: Past, Present and Future

Antonio Feteira, The University of Birmingham, School of Chemistry & The University of Warwick, Department of Physics, UK

Approximately 100 years elapsed between the first report of NTCR behaviour by Michael Faraday and the fabrication of devices exploring this phenomenon. The manufacture of the first NTCR ceramic thermistors was problematic, as often the devices suffered from poor stability and non-reproducibility. Before NTCR ceramics could be seriously considered for mass production of thermistors, it was necessary to devote a large amount of R&D effort to study the nature of their semiconductivity and understand the influence of impurities/dopants and heat treatments on their electrical characteristics, particularly in their time dependence resistivity (aging). Simultaneously, from a technological viewpoint it was important to develop methods enabling reliable and permanent electrical contacts, and design suitable housing for ceramics, in order to preserve their electrical properties under conditions of variable oxygen partial pressure and humidity. Nowadays, there is an increasing need for sensors capable of operating at extreme conditions, in particular at high temperatures (near 1000 °C or above), which sets new challenges in the field of NTCR ceramics.

CH-4:L09 Defect Chemistry of Ba-excess Donor-doped BaTiO3 Thermistor Ceramics

Hayato Katsu*, Christian Pithan, Rainer Waser, Forschungszentrum Jülich, Jülich, Germany

A-site excess and donor-doped BaTiO3 shows a marked positive temperature coefficient (PTC) effect on electric resistivity even when sintered at reduced oxygen partial pressures. However, the origin of this unique PTC effect has not been studied yet. We have employed impedance spectroscopy and the measurement of the pO2-dependence of DC-conductivity to obtain the insights in the physicochemical processes involved in the phenomenon. To realize the PTCR, acceptor states, being responsible for insulating layers at the grain boundaries are considered indispensable. From the view point of defect chemistry, metal vacancies can be one of the candidates responsible for the insulating layer at the grain boundaries in this material system. Impedance spectroscopy measurements show that these PTCR ceramics can be described by the more RC components in the corresponding equivalent circuit with the higher Ba/Ti ratio. Regions with the strongest PTC effect are located in the surface of the ceramics. These observations suggest that the reoxidation process through the grain boundaries is suppressed at the surface of the ceramics. Oxygen diffusion behavior and defect chemistry of metal vacancies during oxidation is discussed through DC-conductivity at the ambience with different pO2 measurement.

CH-4:L10 Structure, Microstructure and Electrical Properties of $Mn_{3-x}Co_xO_4$ (0<x<3) Spinel Ceramics: an Interesting System for Negative Temperature Coefficient (NCT) Thermistors

H. Bordeneuve, Ch. Tenailleau, S. Guillemet-Fritsch*, A. Rousset, Institut Carnot CIRIMAT/UPS/CNRS Université Paul Sabatier, Bât. 2R1, Toulouse Cedex, France; V. Poulain, S. Schuurman, Vishay, Bruxelles, Belgium

The $Mn_{3-x}Co_xO_4$ (0<x<3) spinel oxides represent an interesting system for Negative Temperature Coefficient (NTC) thermistor applications. However, due to the complexity of the phase diagram, only a few studies have been reported in the literature. Dense and single-phase ceramics, especially for the cobalt riche side- the most useful for the applications- are very difficult to elaborate. The use of the Spark Plasma Sintering (SPS) process has allowed the preparation of such ceramics in the cobalt rich domain. In the present work, careful and systematic studies have been performed to establish the relations between the physical properties and the cation distribution in the spinel structure. An original model of cationic distribution based on the difference of reactivity of Co and Mn cations towards oxygen has been proposed, thanks to a submicronic powders thermogravimetric analysis. This model has been confirmed on ceramics of the same composition, using X-ray and neutron diffraction analysis. It shows the presence of both Mn^{3+}/Mn^{4+} and Co^{2+}/Co^{III} couples on the octahedral sites. This double mixed valence allows to explain the low resistivity values (300 Ω.cm) measured in some samples. The fine adjustment of the resistivity and the thermal constant is interesting to expand the application of NTC thermistors to various fields of electronics.

Session CH-5

Optical, Electro-optical and Magneto-optical Ceramics and Devices

CH-5:IL01 Bi-doped Glass Optical Fibers: Properties and Applications

Evgeny Dianov, Fiber Optics Research Center, Moscow, Russia

Since the appearance of the first lasers in 1960 great attention has been paid to the search and the creation of new active laser media. This made it possible to improve the characteristics of the existing lasers and to develop new ones. Active glass optical fibers are one of the most efficient laser media. Until recently there existed only rare-earth-doped fiber lasers, which have found a widespread use in optical communication, medicine, material processing and other applications in the near IR region. But there is a spectral region of 1150-1500nm where in fact no efficient fiber lasers exist. It has been shown recently, that Bi-doped glass optical fibers are a very promising active laser medium. Luminescence of Bi-doped glasses takes place in spectral region of 1150-1500nm. The glasses have very broad luminescence bands (200-400nm) and long lifetime (200-700µs). In this paper the recent results on Bi-doped glasses and optical fibers are reviewed. First, luminescence properties of various Bi-doped glasses are discussed. Then we describe the Bi-doped silica-based optical fiber fabrication and the absorption and luminescence properties of the fibers. At last some results on Bi-doped fiber lasers and their applications are presented.

CH-5:IL02 Ultra-compact Gbps PLZT Electro-optic Modulators on Si Substrate

M. Nakada[1, 2]*, T. Shimizu[1], H. Miyazaki[1], K. Ohashi[1], [1]MIRAI-Selete, Tsukuba, Ibaraki, Japan; [2]NEC Corporation, Tsukuba, Ibaraki, Japan; H. Tsuda, J. Akedo, AIST, Tsukuba, Ibaraki, Japan

Small and low-voltage-driving electro-optic (EO) modulators are expected to become the key technology for chip-to-chip and intra-chip optical interconnects. Practical optical interconnects rely on the development of EO modulators that are integrated with microelectronics on the chip. The modulators on LSI chips are required to be compatible with the silicon CMOS fabrication process. We developed lanthanum modified lead zirconate titanate (PLZT), electro-optic modulators using aerosol deposition (AD). AD enables complex oxide films to be deposited on Si substrates, leading to their possible integration into LSI. Polarization was measured in PLZT optical waveguides that were 1.8 um in width, and ferroelectric hysteresis loops were observed. Mach-Zehnder interferometer (MZI) PLZT modulators were demonstrated with 500-um-length electrodes, and change in the insertion loss of the MZI modulators was observed with applied electric field. Their change in insertion loss exhibited hysteresis loops, which were comparable to their ferroelectric ones. We obtained a 2-GHz optical output signal with a relevant bias voltage.

CH-5:IL03 Abnormal Effects of Sonic Metamaterials

Yan-Feng Chen, National Laboratory of Solid-State Microstructures & Department of Materials Science and Engineering, Nanjing University, Nanjing, China

Sonic crystal, analogous to photonic crystal, has been studied to show some of important effects, such as band-gap, dispersion relation, etc. Very recently, the abnormal phenomena, such as negative refraction, enhanced transmission of acoustic waves in sub-wavelength, and negative bulk modulus and negative mass density, etc., were founded. With these developments, sonic metamaterials have been proposed to parallel to the optic counterpart. In this talk, some of new effects will be presented in artificially designed sonic metamaterials, for example, acoustic tunneling, sonic cloaking, and acoustic surface states. Much less velocity of acoustic wave than light makes it easier to directly measure its amplitude and phase of propagation, and thus provides important compensated evidence to establish basic essences shared by both photonic and sonic metamaterials. Due to the large scale, sonic metamaterials with complicated artificial structures could be easily realized to not only give rise to some novel effects which are difficult to be observed in photonic metamaterials, but also revolutionize the acoustic devices applications.

CH-5:L04 Design, Characterization and Fabrication of Nd3+ Doping Profiles in Transparent YAG Laser Ceramics

R. Gaume*, J.A. Wisdom, R.L. Byer, Stanford University, Stanford, CA, USA

Ceramic gain media with controlled doping profiles offer new potentials to design lasers with enhanced performance in comparison to uniformly doped materials. Here, we propose to discuss some aspects of this new paradigm in solid-state laser engineering. We will first outline different laser geometries that could benefit from doping profiles and then present theoretical and experimental work relative to the fabrication and characterization of these devices. In particular, we will focus on the diffusion mechanisms that constrain the fabrication of arbitrary profiles. As a test case for modeling engineered ceramic gain-media, we will present a novel modeling approach used to optimize transverse doping profile shapes for edge-pumped lasers. Transverse doping profiles can be used in edge-pumped laser geometries to improve coupling of absorbed pump light with a TEM00 beam. Using a genetic algorithm, a doping profile was found that calculations indicate will produce a spot in the far field with a 39% increase in laser power extracted from the slab compared to an optimally designed, uniformly doped slab.

CH-5:L06 Thermal Stability of Ge-Sb-Te Materials for Phase - Change Memory Devices

A.A. Sherchenkov*, Moscow Institute of Electronic Technology, Russia; S.A. Kozyukhin, Kurnakov Institute of General and Inorganic Chemistry, Moscow, Russia

One of the attractive advantages of phase-change memory (PCM) devices is considered to be increased cycling endurance. In this work phase separation in bulk and thin films of (GeTe)m(Sb2Te3)n (m:n=1:1;1:2;2:1), promoting reliability issue were investigated by the multiple differential scanning calorimetry (DSC). For the as-deposited films exo peaks in the temperature ranges 125-190 °C and 200-230 °C were attributed to the transitions from amorphous to fcc structure, and from fcc to the stable hcp phase, respectively. Maxima for both peaks shifted to the lower temperatures with increased Sb2Te3 content. Multiple DSC measurements lead to the appearance of the unknown endo peak in the temperature range 390-415 °C for all compounds. Kinetics of these peaks differs, however coincidence of their positions indicates on the similar origin. Kissinger's method was used for the kinetics analysis. XRD measurements revealed existence of at least two phases after multiple cycling. Appearance of endo peak can be attributed to the low temperature solid state reactions leading to the transformations in Ge-Te sub-lattice and melting of eutectic composition.

This work was supported by a grant 08-03-00651 from RFBR.

CH-5:IL07 Advanced Ceramics for Optical Applications

Jan Ma, School of Materials Science and Engineering and Temasek Labs, Nanyang Technological University, Singapore

Functional ceramics are well accepted to possess many superior properties. Among them, their optical properties have found a wide range of applications in the last decade. Traditionally, single crystal has been widely used for such applications in systems for industrial, medical, scientific and military purposes. However, the requirement for expensive crucibles and the difficulty in growing large size crystal have limited their potential in many advanced applications. With the development of nanocrystalline technology and chemical processing techniques, polycrystalline transparent ceramics have received great attention. Compare to the single crystals, the polycrystalline ceramic have several advantages such as lower cost of manufacture, relatively shorter production time, high homogeneity of the composition, large size and flexible geometry in design. Moreover, multi-layer and multi-functional ceramics can be fabricated by ceramic technology that is impossible by single-crystal growth method. In the present work, the development of transparent polycrystalline ceramics used as solid-state laser materials, and optical limiting materials, were studied. The nature of starting materials such as particle size and morphology, are noted to have significant effects on the forming and sintering process as well as the performance of the resultant product.

CH-5:IL09 Charge Transfer Transitions in 3d Transition Metals Oxides

R.V. Pisarev, Ioffe Physical-Technical Institute, St. Petersburg, Russia

The optical response of multiferroic BiFeO3 and related iron oxides is studied in the wide spectral range of 0.6-5.8 eV by means of spectroscopic ellipsometry[1]. One of the groups of materials with Fe3+ ions in octahedral positions includes BiFeO3, ErFeO3, GaFeO3, Fe3BO6, and others. In the second group Fe3+ ions occupy both octahedral and tetrahedral positions as in LiFe5O8, Ca2Fe2O5 and others. At variance with previous investigations we present a unified assignment of dipole-allowed and dipole-forbidden charge transfer CT transitions. The band gap around ~2 eV or higher is determined by a dipole-forbidden p-d transition in octahedral centers. In the range up to ~3.7 eV the optical response is dominated by allowed p-d CT transitions while at higher energy both p-d and d-d transitions are revealed. The optical response of multiferroic manganite TbMn2O5 shows strong anisotropy which we assign to the on e-center p-d transitions within the Mn3+O5 pyramids. Spectroscopic study revealed a giant coupling of optical second harmonic generation to the magnetically driven ferroelectricity[3].

[1]R.V. Pisarev et al, Phys. Rev. B 79, 235128 (2009); [2]A.S. Moskvin and R.V. Pisarev, Phys. Rev. B 77, 0601102 (2008); [3]Th. Lottermoser et al, Phys. Rev. B 80, 100101 (2009)

CH-5:L10 Development of Highly Sensitive Techniques for Characterizing Optical Gain and Losses in Laser Ceramics

Ye He*, R. Gaume, A. Markosyan, R.L. Byer, Stanford University, Stanford, CA, USA

This work focuses on the development of optical characterization techniques for the evaluation of transparent optical ceramics. These materials present strong potential for laser power-scaling. Such applications however, demand minimal optical loss gain media and high quantum efficiency dopants. This has driven the need for ever improved optical characterization techniques. We have developed techniques to characterize gain, low levels of absorption and scattering using a confocal gain-microscope and a photothermal common-path interferometer (PCI). Here the confocal gain-microscope is adapted to measure the distribution of fluorescence of RE-ions in YAG transparent ceramics with high resolution. One of the unique advantages of this technique over common physical methods, such as SIMS, XPS and EMPA, is the ability to correlate optical defects with final doping profile in micro-engineered transparent ceramics. The PCI allows for the decoupling of scattering and absorption contributions to optical losses. The sensitivity of this technique is as low as 0.1 ppm/cm, which is far more accurate than standard spectrophotometry. At 1064nm, absorption levels one order of magnitude lower than that of Nd:YAG single crystals have been measured in Nd:YAG ceramics.

CH-5:L11 Magnetic and Magneto-Optical Characterization of Diluted Magnetic Colloidal Suspensions

O. Pascu*, J.M. Caicedo, J. Fontcuberta, G. Herranz, A. Roig, Institut de Ciencia de Materials de Barcelona (ICMAB), CSIC, Campus de la UAB, Bellaterra, Catalonia, Spain

Many emergent applications in biomagnetics or magneto-photonic structures require the preparation of monodisperse magnetic nanoparticles in stable colloidal suspensions. Here, we will report on the magneto-optical (MO) measurements of diluted suspensions of magnetic nanoparticles. For that purpose we have prepared colloidal solutions of different concentrations. The MO spectroscopy was done in transmission Faraday configuration at room temperature with a signal proportional to the magnetic circular dichroism (MCD). Using this procedure we have measured the spectral response of the MCD signal as a function of the magnetic concentration in the colloid. We will show that the presented methodology provides an efficient and fast method for functional characterization of extremely diluted magnetic colloidal dispersions and sensitive to size dependent effects. As examples, we will report data on diluted magnetic suspensions of Ni and iron oxide nanoparticles of different sizes, prepared by thermal decomposition of organometallic precursors at high temperature. We will also report on the magnetooptic characterization of some magnetic opals.

CH:P02 Preparation and Characterization of Dielectric Behavior of A2/3Cu3Ti4O12 (A= Nd, Sm, Gd, Dy) Ceramics

D. Szwagierczak*, J. Kulawik, Institute of Electron Technology, Cracow Division, Kraków, Poland

The demand for miniaturization of capacitive elements leads to an enhanced interest focused on new high permittivity nonferroelectric materials, like CaCu3Ti4O12. In this work perovskite materials A2/3Cu3Ti4O12 (where A= Nd, Sm, Gd, Dy) were synthesized by conventional solid state reaction and sintered at 1000-1100° C. X-ray diffraction analysis confirmed single-phase compositions of the investigated ceramics. Dielectric properties of the samples were investigated in the temperature range from -55 to 300 °C at frequencies 10 Hz - 2 MHz. Dielectric permittivities of the ceramics are very high, exceeding 100000 at low frequencies and/or elevated temperatures and 1000 at higher frequencies and/or low temperatures. Two contributions to the dielectric response are attributed to semiconducting grains and more resistive grain boundaries. For Nd2/3Cu3Ti4O12 and Sm2/3Cu3Ti4O12 ceramics, the low- and high frequency plateaus are lower than those for Gd2/3Cu3Ti4O12 and Dy2/3Cu3Ti4O12. The relaxation times were found to decrease with increasing atomic number of lanthanide. The impedance spectroscopic data along with scanning electron microscope observations and X-ray microanalysis imply spontaneous formation of internal barrier layer capacitors in the investigated ceramics.

CH:P04 Microwave Dielectric Properties of Doped Ba(Mg1/3Ta2/3)O3 Ceramics

Cornelia Jinga*, Cristina Jinga, E. Andronescu, S. Jinga, University “Politehnica” of Bucharest, Bucharest, Romania; A. Ioachim, National Institute of Materials Physics, Bucharest-Magurele, Romania

Ba(Mg1/3Ta2/3)O3 (BMT) ceramic is a dielectric material possessing an extremely high Q×f value (more than 400 THz) at microwave frequency. This makes it suitable for applications as a dielectric resonator for wireless communications. The BMT samples, prepared by solid state reaction and doped either with Nb5+, V5+ or Ga3+, were employed for compositional, structural and morphological characterization. In the present study we report on the influence of sintering temperature and dopants (type and quantity) on dielectric properties. It is found that the quality factor is maximum when Nb5+ is used as dopant.

CH:P10 Polydomain Structure in PbTiO3/PbZr0.2Ti0.8O3 Superlattices

C. Hubault*, M.G. Karkut, N. Lemée, Laboratoire de Physique de la Matiere Condensée, Université de Picardie Jules Verne, Amiens, France; L. Dupont, K. Djellab, Laboratoire de Réactivité et Chimie des Solides, LRCS UMR 6007, Amiens, France; A. Perrin, Unité Sciences Chimiques de Rennes, UMR 6226 CNRS/Université de Rennes 1, Campus de Beaulieu, Rennes, France; J. Holc, M. Kosec, Jozef Stefan Institute, Ljubljana, Slovenia

Superlattices based on ferroelectric materials can provide excellent systems to investigate strain and coupling effects on the formation of domain structures. In PbTiO3/SrTiO3 superlattices, the small compressive stress arising from the difference in lattice parameters between SrTiO3 and PbTiO3 at deposition temperature (around -1.1%) results in 180° domains. Combining PbTiO3 with different compositions of the solid solution PbZrxTi1-xO3 in superlattices could provide a way to investigate the effect of the stress on a continuous scale from compressive to tensile. Here we report on the growth and structural characteristics of PbTiO3/PbZr0.2Ti0.8O3 superlattices. Samples were grown by PLD on (001) SrTiO3 substrates. The structural characteristics were studied by X-ray diffraction (reciprocal space map) and by transmission electron microscopy. An a/c polydomain structure was evidenced, resulting from a mechanism of relaxation of internal stresses. This domain structure propagates across the interfaces between individual layers. Superlattices were grown with varying wavelengths and composition ratios so as to modify the stress state and to determine the influence on the characteristics of the domain structure. These results will be analyzed in light of piezoresponse measurements.

CH:P14 Fabrication and Magnetorheological Characteristics of Hollow Fe3O4 Nanoparticles

B.O. Park, B.J. Park, H.J. Choi*, Department of Polymer Science and Engineering, Inha University, Incheon, Korea

Magnetorheological (MR) fluid is a smart suspension of magnetic materials such as carbonyl iron (CI) or iron oxides dispersed in non-magnetic fluid with controllable properties by an external magnetic field[1]. However, CI based MR fluids frequently indicate serious sedimentation problem by its large density, causing drawbacks in their industrial applications. Therefore various efforts such as adding magnetic nanoparticles and coating CI particles have been employed. In this study, we prepared hollow magnetite (Fe3O4) nanoparticles via microemulsion system by hydrothermal method and added into the CI based MR fluid[2]. Morphology and crystal structure of the synthesized hollow Fe3O4 nanoparticles were characterized by scanning electron microscope (SEM) and X-ray powder diffraction, respectively. Rheological characteristics of the MR fluid were measured via a rotational rheometer under various magnetic field strengths. Stability of sedimentation was also evaluated via Turbiscan. The magnetic additive was found to not only influence the yield behavior but also improve sedimentation stability of the MR fluid.

[1] S.T. Lim, M.S. Cho, I.B. Jang, H.J. Choi, J. Magn. Magn. Mater. 282, 170 (2004); [2] F.F. Fang, H.J. Choi, J. Appl. Phys. 103, 07A301 (2008)

CH:P15 Magnetic Properties and High Frequency Response of Single-Phase Z-type Strontium Cobalt Hexaferrite Prepared by Polymerizable Complex Method

T. Kikuchi*, T. Nakamura, T. Yamasaki, University of Hyogo, Himeji, Japan; M. Nakanishi, T. Fujii, J. Takada, Okayama University, Okayama, Japan; Y. Ikeda, Research Institute of Production Development, Kyoto, Japan

Single-phase Z-type strontium cobalt hexaferrite was prepared by the polymerizable complex method. Magnetic properties and dynamic magnetic response for high frequency of the Z-type ferrite were studied. Single-phase Z-type hexaferrite was obtained by heating at 1468K for 5 hours in air. Phase identification and determination of lattice parameters were carried out by powder X-ray diffraction (XRD). Magnetic properties were discussed by measuring of M-H curve with vibrating sample magnetometer (VSM). The complex permeability and permittivity over 0.2-18GHz were measured using an vector network analyzer with transmission-reflection-line (TRL) calibration. The results show that the single-phase Z-type strontium cobalt hexaferrite prepared in this study is one of potential candidates for use as electromagnetic wave absorbing materials in the frequency range 1-3GHz (for hand-held cellular phone and wireless LAN).

CH:P16 Effects of the Co-presence of Conflicting Magnetic Anisotropies in Ba Ferrite Particles

G. Bottoni, Dept. of Physics, University of Ferrara, Ferrara, Italy

Ba ferrite particles are used in particulate recording media. At this aim, they are often modified with ionic additions. In hexagonal Ba ferrite particles both magnetocrystalline and shape anisotropies are contemporarily present and conflicting: the crystalline easy axis (c) is hard axis for the shape anisotropy of the platelet-like particle and vice versa. In this work the strength and evolution of the anisotropies are studied, and the effect on the basic magnetic behaviour analyzed. In undoped Ba ferrite particles the crystalline anisotropy prevails on shape anisotropy both at room and low temperatures, which results in a uniaxial anisotropy. When the particles are modified, the crystalline anisotropy is weaker and close to the shape anisotropy, which easy plane is in the platelet plane. Particularly this occurs at low temperature, where the shape anisotropy constant can exceed the crystalline constant. It should result in a cone of easy magnetization, but the matter is even more complicated by the irregular bases of the particles, which give rise to additional preferred directions for magnetization. This presence of multiple anisotropy axes will affect, besides the macroscopic magnetic properties, also the switching and thermal stability of the magnetization of the particles.

CH:P17 In-situ Measurement of Phase Transition of Layered Perovskite BaLn2Mn2O7

Hiromi Nakano[1], Nobuo Ishizawa[2], Hirohisa Satoh[1], Naoki Kamegashira[1]*, [1]Toyohashi University of Technology, Toyohashi, Japan; [2]Nagoya Institute of Technology, Japan

The BaLn2Mn2O7 (Ln = rare earth) has a Sr3Ti2O7-type structure with double block oxygen octahedra belonging to the Ruddlesden-Popper-Type homologous series AO(ABO3)2. In-situ measurement of the phase transition for BaLn2Mn2O7 was performed using single-crystal X-ray diffraction and a high-temperature transmission electron microscope (TEM). Two types of transitions were observed in BaPr2Mn2O7: the transition from primitive tetragonal (P42/mnm) to body-centered tetragonal (I4/mmm) at around 400 K and the first-order phase transition at around 1040 K. Multiple phase transitions were also observed in BaEu2Mn2O7, with one from P42/mnm to I4/mmm at around 400 K and another, above 550 K, as a first-order phase transition. The high-temperature phase had a 1.5% lattice mismatch along the c-axis compared with the low-temperature phase. We succeeded in recording for the first time in-situ structural change in BaGd2Mn2O7 as a movie by high-temperature TEM. The high-temperature phase nucleated parallel to the (00l) plane as a layer above 550 K and grew until covering the entire inspected region at around 1023 K. The first-order phase transition was caused by the structural and/or electrical distortion of the layered perovskite structure composed of Jahn-Teller ion Mn3+.

CH:P19 **Simplified Method of Measuring Magnetic Permeability Temperature Profile for RF Device Applications**
Atsushi Kuramoto[1], Takanobu Aoyama[2], Tomohiko Kanie[3], Yuichi Noro[1], Takashi Takeo[1]*, [1]Mie University, Tsu, Mie, Japan; [2]Tokai Polytechnic College; [3]Aoyama Technology, Japan

Ferrite is a popular magnetic material used in various industrial components such as RF devices. For example, a widely used RF transformer includes ferrite as its core. One of the parameters that dominate the above mentioned device's performance is the magnetic permeability. Since the electronic devices in operation are subject to a considerable temperature change, it is very important to know or measure the temperature profile of the ferrite permeability so as to design the performance of such RF devices using ferrite. In this study, we investigate a simplified method, which employs microstrip line circuits, for measuring the ferrite permeability temperature profile in a frequency range of MHz to GHz. Since the measurement circuits of the present method are small in size, it is suitable for the temperature profile measurement. After presenting the measurement results of the ferrite material itself obtained with this method, we will discuss the temperature characteristics of RF devices utilizing ferrite as their component with a view to examining the validity of the method. A method for compensating the temperature variation of the device performance by electrically controlling the material permeability may also be investigated.

Focused Session CH-6

MULTIFERROICS

Oral Presentations

Session CH-6.1
Theory and Modeling of Materials and Phenomena

CH-6.1:IL01 **Dynamical Magnetoelectric Effects in Multiferroic Oxides**
Yoshinori Tokura, Department of Applied Physics, Universityo of Tokyo; ERATO Multirferroics Porject, JST, Japan

Multiferroics with coexistent ferroelectric and magnetic orders can provide an interesting laboratory to test unprecedented magnetoelectric responses and their possible applications. One such example is the dynamical and/or resonant coupling between the magnetic and electric dipoles in a solid. Here, as the examples of such dynamical magnetoelectric effects, (1) the multiferroic domain wall dynamics and (2) the electric-dipole active magnetic responses are discussed with the review of recent experimental observations.

CH-6.1:IL02 **Symmetry and Mechanisms for Magnetically Driven Ferroelectricity**
J.L. Ribeiro, Departamento de Física, Universidade do Minho, Braga, Portugal

The complete irreducible co-representations of the paramagnetic space group provide a simple and direct path to explore the symmetry restrictions of magnetically driven ferroelectricity. The method consists of a straightforward generalization of the one commonly used in the case of displacive modulated systems and allows us to determine, in a simple manner, the full magnetic symmetry of a phase originated from a given magnetic order parameter. The potential ferroic and magneto-electric properties of that phase can then be established and exact Landau free energy expansions can be derived from general symmetry considerations. The specific example of the orthorhombic rare-earth manganites RMnO3 will be used to stress some aspects related to the multi-ferroic properties of this class of frustrated magnets and to emphasize points such as the role played by the magneto-elastic and magneto-electric coupling in the stabilization of ferroelectricity, the essential differences between commensurate and incommensurate modulations regarding the ferroic and magneto-electric properties or the possible onset of an improper polarization due to one irreducible magnetic order parameter. Possible mechanisms for the polarization rotation induced by an external magnetic field will also be discussed.

CH-6.1:IL03 **First Principles Study of the Magneto-electric Coupling and Phase Diagrams of Multiferroic RMn2O5**
Lixin He, Key Laboratory of Quantum Information, University of Science and Technology of China, Hefei, Anhui, China

RMn2O5 (R=Tb, Dy, Ho, Y etc.) belong to a very special class of multiferroics, because the ferroelectricity is driven by the magnetic ordering. To clarify the microscopic origin of the ferroelectricity and strong magnetoelectric coupling in these materials, we investigate the structural, electronic and magnetic properties of these compounds via first-principles calculations. We determined the lattice and magnetic structure of the materials, calculated the electric polarization. We show that the ferroelectricity in these materials is due to the "exchange striction" effects. We further derived an effective Hamiltonian. Using this Hamiltonian with parameters determined from first-principles calculations, we obtained the most important features of the phase diagrams of RMn2O5 compounds, including the sequence of magnetic and ferroelectric phase transitions. Most importantly, we obtained the dielectric-constant step at the commensurate-to-incommensurate magnetic phase transition, which is key to understand the colossal magneto-dielectric effects.

CH-6.1:IL04 **Magnetic Switching of Relaxor Ferroelectrics: Theory**
R. Pirc*, R. Blinc, J. Stefan Institute, Ljubljana, Slovenia; J.F. Scott, Cavendish Laboratory, Cambridge, UK

Recent experiments on thin films 0.2PFW/0.8PZT revealed a critical magnetic field dependence of the dielectric relaxation time tau[1], which was found to obey a magnetic Vogel-Fulcher-type law with a critical field Hc~0.9 T. On approaching Hc, dielectric hysteresis loops collapse to the horizontal axis: this is equivalent to switching the polarization P to zero by the magnetic field. Here we discuss a theoretical model of birelaxors, i.e., systems which possess both relaxor ferroelectric and relaxor ferromagnetic properties, assuming that polar nanoregions (PNRs) and magnetic nanoregions (MNRs) interact with lattice strains via electrostriction and magnetostriction coefficients. This leads to a 4-th order magnetoelectric (ME) coupling term between P and magnetization M in the Landau-type free energy. We then study the effects of both electric (E) and magnetic (H) bias fields on tau by adopting the mechanism of growth and percolation of PNRs, and show that tau diverges on a critical surface in the E,H,T space. For E=0, H>0 we derive tau(H), which agrees with the empirical relation[1]. For E>0, H=0 we obtain a similar result for tau(E), which is also applicable to relaxor ferroelectrics without ME coupling.

[1] *A. Kumar et al, J. Phys.: Cond. Matter 21, 382204 (2009).*

CH-6.1:IL05 Ferroelectric and Multiferroic Tunnel Junctions: Insight from Theory

Evgeny Y. Tsymbal, Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska, USA

Tunnel junctions are electronic devices in which current-carrying electrons can quantum-mechanically be transmitted between two metal electrodes across a very thin insulating barrier layer. So far almost all the existing tunnel junctions are based on non-polar dielectrics. An exciting possibility to extend the functionality of tunnel junctions is to use a ferroelectric insulator as a barrier to make a ferroelectric tunnel junction (FTJ).[1] The key property of FTJ is tunneling electroresistance (TER) that is a change in the electrical resistance of FTJ with reversal of ferroelectric polarization. Functional properties of FTJ can be extended by replacing normal metal electrodes by ferromagnets. In such a multiferroic tunnel junction (MFTJ) spin-dependent tunneling may be controlled by ferroelectric polarization of the barrier.[1] This implies that by switching the ferroelectric polarization one can affect tunneling magnetoresistance (TMR). MFTJs represent four-state resistance devices that can be controlled both by electric and magnetic fields due to the coexistence of TER and TMR effects. This talk will address the physics of FTJs and MFTJs based on our recent model and first-principles calculations.

[1] *E.Y. Tsymbal and H. Kohlstedt, Science 313, 181 (2006)*

CH-6.1:IL06 Static and Dynamic Magnetoelectric Effects in Magnets with Non-collinear Spin Orders

M. Mostovoy, Zernike Institute for Advanced Materials, University of Groningen, Groningen, The Netherlands

The orthorhombic rare earth manganites, RMnO3 and RMn2O5, show competing commensurate and incommensurate spin orders, both of which are ferroelectric. This competition has important implications for the dynamic magnetoelectric coupling between spin waves and polar phonons, resulting in mixed electromagnon excitations. I will present theory of single-magnon and bi-magnon excitations by an electric field of light, which explains electromagnon peaks recently observed in orthorhombic manganites. I will discuss applications of this theory to other non-collinear magnets, such as the layered triangular and Kagome antiferromagnets carrying monopole or toroidal magnetic moments and exhibiting a linear magnetoelectric effect. The frequencies of electromagnon peaks in these materials coincide with the frequencies of antiferromagnetic resonances and the ratio of the spectral weights of the electromagnon and antiferromagnetic resonance is related to the ratio of the static magnetoelectric constant and magnetic susceptibility. I will also discuss other materials where electromagnons can be observed.

CH-6.1:IL07 Probing Chirality in Multiferroic Manganite Perovskites

Dimitri N. Argyriou, Eugen Weschke, Enrico Schierle, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany

The structure and dynamics of domains and domain walls are at the heart of any device that utilizes the properties of a ferroic material. Magneto-electric (multiferroic), materials exhibit a strong coupling between ferroelectric and magnetic order, offer the possibility of rich and complex domain arrangement that can be exploited for spintronics and magneto-electric devices. Due to the complex magnetic order that is found in multiferroics, imaging of domains of a composite ferroic nature is challenging. In perovskite manganites such as REMnO3 (RE=rare earth) a magneto-electric coupling results from a cycloidal Mn magnetic order. Such order can have opposite chirality which results in ferroelectric polarization of opposite sign. Using soft X-ray scattering methods we have developed a means to probe the chirality of the magnetic order on the surface of cleaved single crystals. We are able to imprint locally domain boundaries and subsequently read them in terms of their spin chirality. The method we describe here provides for a novel approach to probe complex domains in chiral magneto electric materials.

Session CH-6.2
Advances in Materials Synthesis and Processing

CH-6.2:IL01 Multiferroicity due to Charge Ordering

Jeroen van den Brink, Leibniz Institute IFW Dresden, Germany

We focus on multiferroicity driven by different forms of charge ordering and will present the generic mechanisms by which charge ordering can induce ferroelectricity in magnetic systems. On the basis of both ab initio bandstructure and model calulations we observe that is a number of specific classes of materials for which this is relevant. We will discuss (i) perovskite manganites of the type (PrCa)MnO3 close to and at half-doping, (ii) double perovskites such as Y2NiMnO6 (iii) manganites of the type RMn2O5 (iv) rare earth nickelates of the type RNiO3 and (v) possible multiferroicity in TTF-CA organic molecular crystals. From first principles we find magneticaly induced ferroelectric polarizations in the order of few µC/cm2. By analyzing a model Hamiltonian we can understand the microscopic origins of such large polarizations and show that, at least theoretically, in particular materials an external electric field can be used to tune the magnetic phase transition, thus in principle allowing electrical control of the magnetization.

CH-6.2:L02 Synthesis and Characterization of Aurivillius Phase Thin Films

L. Keeney*, P. F. Zhang, Tyndall National Institute, "Lee Maltings", Prospect Row, Cork, Ireland; C. Groh, Materials Science Department, Friedrich Schiller University of Jena, Germany; M.E. Pemble, R.W. Whatmore, Tyndall National Institute, "Lee Maltings", Prospect Row, Cork, Ireland

Aurivillius bismuth-based compounds represent an important class of piezoelectric compounds having the potential to present both ferroelectric and magnetoelectric transitions at the same time in a single phase. The materials are members of a homologous series of Bi-layered oxides, consisting of (Bi2O2)2+ layers alternating with nABO3 perovskite units, described by the general formula Bi2O2(An 1BnO3n+1). On increasing the number of perovskite layers (n), the microstructural, magnetic and physical properties of the materials can be altered significantly. Chemical doping of perovskite type materials has been useful in enhancing electrical and magnetic properties. We describe chemical solution deposition (CSD) and characterization of n ≥ 3 Aurivillius phase thin films. The number of perovskite layers was increased by inserting BiFeO3 perovskite layers into three layered Aurivillius phase Bi4Ti3O12 to form compounds such as Bi5FeTi3O15 (n = 4). B site cations were doped with magnetic ions such as Mn3+ and Co3+. Novel liquid injection atomic vapour deposition (AVD) routes were examined as alternative thin film preparation processes. Electromechanical and magnetic behaviour of the materials were investigated and the results are discussed in relation to the crystallinity of the films.

Session CH-6.3
Magnetoelectric Characterization

CH-6.3:L01 Large Ferroelectric and Magnetic Hystereses coexisting in BiFeO3 Thin Films

Masanori Okuyama*, Jung-Min Park, Takeshi Kanashima, Osaka University, Graduate School of Eng. Science, Dept. of Systems Innovation, Toyonaka, Japan

Multiferroic BiFeO3 (BFO) is well known to have an excellent ferroelectric property, which shows giant ferroelectric polarization (Pr ~152 uC/cm2) at 80K in thin film form, but still serious problems such as low insulation and poor ferromagnetism remain. Also there have been few reports on coexistence of ferroelectric and magnetic hystereses. In this work, good ferroelectric and magnetic hystereses have been simultaneously obtained in the BFO thin films by co-substitution of Bi and Fe with Sr and Zn, respectively. Thin films were deposited on Pt /TiO2 /SiO2 /Si (625 um) substrate by pulsed laser deposition using ceramic targets of Bi1.1SrxFeO3 (BSFO), Bi1.1Fe0.9ZnxO3 (BFZO) and Bi1.1SrxFe0.9Zn0.1O3 (BSFZO) (x=0, 0.5 and 0.1). Obtained films are 350-nm-thick and rhombohedral. M-H curve in the BSFO film is improved with increasing Sr, although insulation property is not improved. Enhancement of the remanent magnetization is considered to be due to deformation of lattice structure by substituting Bi with Sr of large ion radius. Leakage current in the BFZO film is suppressed by substitution with Zn. Insulation improvement is considered to be due to reduction of defect states induced by substituting with divalent Zn. Moreover, the BSFZO films show simultaneously good ferroelectric and magnetic hystereses. Remanent polarization and remanent magnetization obtained in Bi1.1Sr0.1Fe0.9Zn0.1O3 film at 80K are 58uC/cm2 and 6emu/cc, respectively.

CH-6.3:L02 Magnetic and Electric Relaxor Behavior and Spin Lattice Coupling in Epitaxially Grown Multiferroic 0.8Pb(Fe1/2Nb1/2)O3-0.2Pb(Mg1/2W1/2)O3 Thin Films

W. Peng, N. Lemée, J.L. Dellis, M.G. Karkut*, LPMC, University of Picardy Jules Verne, Amiens, France; V.V. Shvartsman, P. Borisov, W. Kleemann, Angewandte Physik, University Duisberg-Essen, Duisberg, Germany; Z. Trontelj, J. Holc, M. Kosec, R. Blinc, Jozef Stefan Institute, Ljubljana; B. Dkhil, SPMS, Ecole Centrale Paris, Châtenay-Malabry, France

Levstik *et al*[1] reported ferroelectric and magnetic relaxor-like properties in a ceramic solid solution of 0.8Pb(Fe1/2Nb1/2)O3-0.2Pb(Mg1/2W1/2)O3 (PFN-PMW). Their results demonstrate magneto-electric coupling, not by long range order, but by local polar and magnetic nanoclusters. Here we report on the growth, structural, electric and magnetic characterization of epitaxial films of PFN-PMW grown by pulsed laser deposition[2]. We observe frequency dispersion of the dielectric permittivity with a freezing temperature of 270K. Hysteresis loops confirmed the ferroelectric character of the films. We observe pronounced irreversibility between the field-cooled and the zero-field-cooled dc magnetization along with a cusp in the ZFC curve at 40K, a characteristic of spin glass or cluster glass systems. The magnetic ac susceptibility exhibits frequency dispersion with freezing at 36K for which we also observe an anomaly in the film lattice parameter providing evidence for spin-lattice coupling. M-H hysteresis loops confirm the existence of magnetic relaxation. The hysteresis persists up to 300K and we attribute superantiferromagnetic clusters to be at the origin of this weak ferromagnetism.

[1]A. Levstik et al, Appl. Phys. Lett. 91 (2007) 012905; [2]W. Peng et al, Appl. Phys. Lett. 95 (2009) 132507

CH-6.3:L04 **Control Magnetization Electrically Using LSMO/BFO Heterostructures**

Lu You, Junling Wang*, School of Materials Science & Engineering Nanyang Technological University, Singapore

Multiferroics, defined as materials that possess at least two of the ferroic (electric, magnetic and elastic) properties simultaneously, have attracted tremendous attention recently. Among them, materials that show both ferroelectricity and magnetic order are especially attractive, because of the possibility of controlling magnetism with electric field. They can be used in spintronic devices and high density data storage systems. As the only room temperature multiferroic material, BiFeO3 has been the focus of this area. Despite intensive research, it is still challenging to obtain high quality BiFeO3 thin films. In this talk, I will discuss the effects of different parameters during pulsed laser deposition (PLD). It was observed that oxygen partial pressure affects the domain structure and defects of the film significantly. We have also studied the magnetic properties of ferromagnetic (LaSr)MnO3 / antiferromagnetic BiFeO3 heterostructures. Large enhancement in the coercive field of the (LaSr)MnO3 is observed, indicating the existence of strong exchange coupling. The ferroelectric domain structure of BiFeO3 affect the magnetic responses of (LaSr)MnO3. The possibility of controlling magnetization electrically using such a heterostruture will be discussed.

Session CH-6.4
Dynamics of Multiferroics

CH-6.4:IL02 **Electromagnons in Perovskite Manganites**

Andrei Pimenov, Universitaet Wuerzburg, Wuerzburg, Germany

Static and dynamic properties of multiferroics are closely connected via the first principles. This leads to the existence of characteristic magnetoelectric excitations called electromagnons. The basic difference of the electromagnons from the “conventional” magnons (e.g. antiferromagnetic resonances) is their ability to strongly interact with the electric field of light. I will present the current state of the art in the terahertz spectroscopy of the electromagnons and discuss the applicability of different models to explain various effects observed in experiment.

CH-6.4:IL03 **Electric Modulation of Exchange Anisotropy in Multiferroic-ferromagnetic Heterostructures**

M. Gajek[1,3]*, J. Heron[2], C-H. Yang[1], Y. H. Chu[5], L. W. Martin[4], R. Ramesh[1,2], [1]Dept. of Physics, University of California at Berkeley, Berkeley, CA, USA; [2]Dept. of Materials Science, University of California at Berkeley, Berkeley, CA, USA; [3]Dept. of Electrical Engineering and Computer Science, University of California at Berkeley, Berkeley, CA, USA; [4]Dept. of Materials Science and Engineering, University of Illinois at Urbana-champaign, Urbana, IL, USA; [5]Dept. of Materials Science and Engineering, National Chiao Tung University, Hsin Chu, Taiwan, ROC

Magnetic switching without a magnetic field is an active research topic in spintronics with important technological repercussions. Several approaches towards this goal are currently being explored in the community, most notably spin torque based switching. An alternative route is to use magnetoelectric multiferroics with cross-coupled ferroelectric and antiferromagnetic orders. When in contact with a multiferroic a ferromagnet displays an exchange anisotropy which can then be modulated electrically. We show that switching the electric polarization triggers a magnetization reversal in the BiFeO3/CoFe system at room temperature. We will discuss the origin of the coupling as well as the mechanisms involved in the switching of magnetization and devices based on this phenomenon.

CH-6.4:L04 **Strain Induced Ferroelectricity in Antiferromagnetic EuTiO3 Thin Film**

S. Kamba*, V. Goian, M. Kempa, V. Bovtun, Institute of Physics ASCR, Prague, Czech Republic; J.H. Lee, D.G. Schlom, C.J. Fennie, Cornell University, Ithaca, New York, USA

Quantum paraelectric EuTiO3 exhibits sharp drop down of permittivity at antiferromagnetic phase transition near 5.3 K and a 7% increase of permittivity with external magnetic field. This gives evidence about a large spin-lattice coupling in this system. Giant magnetoelectric coupling was proposed from the first principles in EuTiO3 thin films, where the ferroelectric and simultaneously ferromagnetic phase could be induced by a strain. We have investigated infrared reflectivity spectra of +1% tensile strained EuTiO3 film deposited by reactive molecular-beam epitaxy on a (110) DyScO3 substrate. Analysis of the infrared spectra revealed a ferroelectric soft mode exhibiting minimum frequency at 250 K. At the same temperature the microwave permittivity maximum was observed. This gives the evidence about the ferroelectric phase transition at 250 K. Moreover, other new phonon modes activate near 150 K due to the antiferrodistortive phase transition. The spectra also reveal the coupling of the soft TO1 Slater mode (Ti-O6 vibration) with the Last TO2 mode (Eu vibration against TiO6) due to Eu-O-Eu super-exchange interaction. This is responsible for the large magnetocapacitive effect in EuTiO3 reported previously. Study of the magnetoelectric effect is in progress.

CH-6.4:IL05 **Soft X-ray Spectroscopic Investigations on Multiferroic Oxides**

Jae-Hoon Park, POSTECH, Pohang, Korea

Recently, multiferroicity takes much attention due to its exotic magnetoelectric effects resulting from cross-coupling between magnetism and ferroelectricity. The ferroelectricity is induced by the off-centering of charges, which naturally contributes the orbital anisotropy and non-vanishing orbital angular momentum. In the multiferroicity, the spin-orbit (LS) coupling, a relativistic quantm effect, is a key factor for the intercoupling electromagnetic phenomena. Here I will discuss microscopic investigation on the orbital and spin anisotropy in various multiferroic Mn and Fe based oxides by using synchrotron based spectroscopic techniques such as soft x-ray absorption spectroscopy (XAS), magnetic circular dichroism (XMCD), and resonant scattering (SXRS). These techniques provide direct information on the electronic structure, the bonding anisotropy, the orbital and spin angular momenta, and the spin ordering structures, which are very essetial for understanding the fundamental mechanism and origin of various cross-coupling phenomena observed in the multiferroic oxides.

CH-6.4:IL07 **Piezoelectric Control of Magnetic Properties in Thin Film Heterostructures**

K. Dörr*, A.D. Rata, A. Herklotz, O. Bilani-Zeneli, M.C. Dekker, L. Schultz, IFW Dresden, Dresden, Germany; M. Reibold, Triebenberglabor, TU Dresden, Germany; M.D. Biegalski, H.M. Christen, Oak Ridge National Laboratory, Oak Ridge, TN, USA

We perform the electrical control of uniform strain in eptaxially grown magnetic films and multilayers on piezoelectric 0.72Pb(Mg1/3Nb2/3)O3-0.28PbTiO3(001) (PMN-PT) substrates. Thorough structural investigations have been conducted by four-circle x-ray diffraction and high-resolution transmission electron microscopy. Results demonstrate the reversible, approximately linear, uniform film strain that allows the direct measurement of strain-dependent properties. This way, the strain dependences of the magnetization (M) and the electrical conductivity (C) have been investigated for ferromagnetic (La,Pr)1-xAxMnO3 (A = Sr; Ca; x = 0.2-0.3) and La1-xSrxCoO3 (x = 0; 0.18; 0.3). Manganites known for their colossal magnetoresistance also show huge responses to reversible strain in both M and C[1]. Cobaltites raised the hope for tuning the Co spin state (magnetic moment) by strain. The strain response of M in LaCoO3 is found to be consistent with spin state control, whereas for x > 0.17 the bandwidth control by strain is dominating. A strain-induced insulator state is observed in the doped films (x = 0.18; 0.3) under tensile strain[2], the microscopic origin of which will be discussed.

[1]C. Thiele, PRB 75, 054408; M.C. Dekker, PRB 80, 144402; [2]A.D. Rata, PRL 100, 076401

CH-6.4:IL08 **Magnetic Excitations in Multiferroics: an Inelastic Neutron Scattering Study**

M. Braden, II. Physikalisches Institut, University of Cologne, Cologne, Germany

The question of a hybridized phonon-magnon mode, called electromagnon, has attracted considerable interest since the first report for TbMnO3 by optical techniques. We have analyzed the magnetic excitations in three families of multiferroic materials using inelastic neutron scattering: TbMnO3, MnWO4 and NaFeSi2O6. In all these compounds there is a strong frustration of magnetic interaction visible in agreement with the observed incommensurate magnetic structures. The most detailed analysis can be made for TbMnO3, where it is possible to unambiguously determine those magnon modes which posses the polarization expected for the electromagnon. The energy of one of these modes perfectly agrees with that of the lowest electromagnon feature observed in the optical spectra over the entire temperature range, but the totality of the optical response apparently bases on different mechanisms.

Session CH-6.5
Structural Characterization and Spin Order of Multiferroics

CH-6.5:IL01 **Magnetically-induced Electric Polarziation in a Collinear Oxide Antiferromagnet and in an Organo-metallic Quantum Magnet**

M. Kenzelmann, Paul Scherrer Institute, Villigen-PSI, Switzerland

Magnetic insulators with competing exchange interactions can give rise to strong fluctuations and qualitatively new ground states. The proximity of such systems to quantum critical points can lead to strong cross-coupling between magnetic long-range order and the nuclear lattice. One such example is the class of magnetically-induced ferroelectrics. I will talk about recent experiments on two different types of materials. Firstly, I will present our results of a collinear oxide antiferromagnet with a possibly large ferroelectric polarization. Secondly, I will talk about a magneto-electric organo-metallic material where ferroelectric polarization emerges at a quantum critical point and the magneto-electric interactions are mediated by large molecules.

CH-6.5:IL02 **Structure, Electrical and Magnetic Properties of Hexagonal ReMnO3 Heterostructures**

C. Dubourdieu*, I. Gelard, H. Roussel, LMGP, CNRS, Grenoble INP, Grenoble, France; S. Pailhes, LLB, CNRS-CEA, CEA Saclay, Gif-sur-Yvette, France; N. Jenathan, O. Lebedev, S. Van Tendeloo, EMAT, University of Antwerp, Antwerpen, Belgium

Hexagonal RMnO3 heterostructures (R=Tb, Dy, Ho, Er and Y) were grown by MOCVD on (111) YSZ and Pt-buffered Si substrates. The crystalline structure of the films was studied by x-ray diffraction. The films grow epitaxial on (111) YSZ and locally epitaxial on Pt grains. TbMnO3 and DyMnO3 are obtained in the hexagonal structure by epitaxial phase stabilization. The films grow in a two-layer scheme, with a strained layer at the interface with the substrate and a relaxed layer on top of it. The critical thickness is of ~25 nm. The effect of the cationic composition on the microstructure, particularly on the defects (as observed by TEM), and on the lattice parameters will be discussed. The electrical properties of the films were studied on MOS structures prepared from the Pt-buffered Si stacks. A dielectric permittivity of 20 was determined on YMnO3 films. The effect of the cationic composition and of the rare-earth element on the leakage currents was investigated. An increase of the leakage current with decreasing ionic radius of the rare-earth is observed. Finally, the magnetic properties of the films and of (YMnO3/ErMnO3)n multilayers will be presented. Antiferomagnetism was evidenced in YMnO3, HoMnO3 and ErMnO3. The effect of film thickness on TN and domain size will be discussed.

CH-6.5:IL03 **Magnetoelectronic Coupling in Frustrated Spin Systems**

Thomas T.M. Palstra, Zernike Institute for Advanced Materials University of Groningen, The Netherlands

Multiferroic and magnetoelectric compounds allow coupling between the magnetic and electric moments. We have investigated several classes of materials with frustrated spin systems such as spinels, hexagonal manganites and jarosites. The frustration allows a large variation in spin-structures and moreover a large spin-susceptibility at low temperature. Utilizing the symmetry of the system, many aspects of the coupling can be well described by a Landau expression of the free energy, including coupling parameters and critical behavior of the magnetocapacitance. For many systems the microscopic coupling constants are small, especially if the coupling originates from spin-orbit coupling of antisymmetric superexchange. We have analyzed some systems, including a jarosite, where the coupling may originate from superexchange induced striction. Here, the coupling constants can, in principle, be orders of magnitude larger.

CH-6.5:L04 **Evidence for a Monoclinic alpha - Monoclinic beta First- Order Transition in BiFeO3 Thin Films**

H. Toupet, F. Le Marrec*, M.G. Karkut, LPMC, Université de Picardie Jules Verne, Amiens, France; C. Lichtensteiger, DPMC, Université de Genève, Genève, Switzerland; B. Dkhil, SPMS, Ecole Centrale Paris, Châtenay-Malabry, France

Among the few room temperature single-phase multiferroics, BiFeO3 is the most studied both in bulk and in thin film form. Despite extensive structural studies on bulk BiFeO3, controversial and unresolved issues concerning the high temperature phases still remain: the symmetry of the paraelectric β-phase is currently subject of debate, and the occurrence and nature of a β–γ phase transition is an open question. In thin films, studies at high temperatures on epitaxial BiFeO3 have been rare due to the chemical instability of the compound. We have found a way to overcome this degradation problem in epitaxial thin films grown by pulsed laser deposition and hence have been able to make a reliable determination of both the order of the α–β phase transition and the symmetry of the β-phase using high resolution x-ray diffraction. We find that BiFeO3 undergoes two high temperature transitions: a first order α–β phase transition between 745 °C and 780 °C and a more diffuse transition toward the γ-phase at 860 °C. Reciprocal space maps reveal that the thin films remain monoclinic in crossing the α–β phase boundary. Linear extrapolation of the in-plane lattice parameters to higher temperatures appears to rule out cubic symmetry for the γ-phase.

Session CH-6.6
New Effects

CH-6.6:IL01 **Electromagnons in Multiferroics**

Dennis Drew, CNAM, Physics, University of Maryland, College Park, MD, USA

In multiferroic materials simultaneous magnetic and ferroelectric order are observed. They have attracted much attention recently because of the fundamental interest of systems with coupled order parameters and because of their potential for cross electric and magnetic functionality in electronics and information storage and processing. These materials also exhibit novel coupled magnon-phonon excitations called electromagnons. These are magnons that can be excited by the electric field of the electromagnetic wave so that electric dipole spectral weight is transferred from the phonons down to the magnon frequency. Electromagnons therefore provide a mechanism for enhancing the static dielectric constant and can produce a magneto-capacitance. Electromagnons have been observed in ortho-RMnO3 and RMn2O5 compounds (R=rare Earth). The phenomenology of electromagnons will be reviewed. I will address the question of the mechanisms for coupling magnons to the phonons. As it happens the mechanism for electromagnons is not always the same as the mechanism for multiferrocity. This raises the possibility that electromagnons are more general than multiferroicity. I will also discuss the generalization of electromagnons to non-polar phonons.

CH-6.6:IL02 **Novel and Original Features on the Model Multiferroic BiFeO3 Under Strain Effects**

Brahim Dkhil, UMR-8580 Ecole Centrale Paris - CNRS, Chatenay-Malabry, France

Despite the tremendous effort devoted to the study of the model BiFeO3 (BFO) multiferroic system, a number of important questions, especially when BFO is deposited as a thin film, still remains unresolved. After highlighting the complexity of the still debated and unclear phase diagram of BFO, this talk will focus on our recent results obtained on BFO thin films by combining several advanced experimental and theoretical approaches. Under strong tensile strains, the structure finds an unusual strain-accommodation mechanism with a rotation of the in-planunit cell axis by 45° with respect to the substrate ones, while under strong compressive strains, unexpected monoclinic phases are obtained despite giant-tetragonality. Interestingly, our data demonstrate the key role played by the oxygen octahedra tilts, which are usually neglected, while this structural degree of freedom is very common to perovskite structure. Under strain, both the polar displacements and the -usually neglected- oxygen octahedra tilts compete and we found that tilts fight against the polarization. This original finding allows to explain the weak enhancement of the polarization reported in the literature and brings a comprehensive view which should be taken into account in a larger manner in multiferroics.

CH-6.6:IL03 **Multiferroic Phenomena in Charge Ordered Manganites**

V.S. Amaral*, F. Figueiras, Depto de Física and CICECO, Universidade de Aveiro, Aveiro, Portugal; I.K. Bdikin, A.L. Kholkin, Depto de Engenharia Cerâmica e Vidro and CICECO, Universidade de Aveiro, Aveiro, Portugal; A.M.L. Lopes, CFNUL, Lisboa, Portugal; J.P. Araújo, Depto de Física and IN-IFIMUP, Universidade do Porto, Porto, Portugal; J.G. Correia, CERN EP, Geneva, Switzerland and Instituto Tecnológico Nuclear, E.N. 10, Sacavém, Portugal; Y. Tomioka, CERC, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan; Y. Tokura, Dept. of Applied Physics, University of Tokyo, Tokyo, Japan

Electrical polarization at local scale was observed near the charge-order (CO) transition in Pr1 xCaxMnO3 manganites using radioactive hyperfine techniques that allow the measurement of the electric field gradient at the local probe [Lopes *et al*, PRL 100, 155702 (2008)]. This finding confirms predictions of CO breaking inversion symmetry, leading to multiferroic behaviour. Piezoresponse Force Microscopy (PFM) technique allows measurements of local hysteresis loops at 10 nm level by detection of local piezoelectric deformation induced by an external electric field. We also report the observation of bias-field induced ferroelectricity in these complex manganites using PFM. We could induce and further study clear piezocontrast zones which may be associated with the presence of nanoscopic CO regions (above the macroscopic CO transition) after the application of a voltage. This possibility of producing single domain electronic phase transitions opens a new pathway to achieve local multiferroic studies, and widens the possibilities of high density applications.

CH-6.6:IL05 **Magnetoelectric Multiglass Ceramics (Sr,Mn)TiO3 and (K,Mn)TaO3**

W. Kleemann*, V.V. Shvartsman, P. Borisov, S. Bedanta, Angewandte Physik, Universität Duisburg-Essen, Duisburg, Germany; A. Tkach, P. M. Vilarinho, Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, Aveiro, Portugal

By analogy with the well-known multiferroics a “multiglass” situation is encountered with two co-existing different glass states in the ceramic system Sr_0.98Mn_0.02TiO_3. Owing to a special growth strategy Mn ^ 2+ ions are forced to randomly occupy Sr ^ 2+ lattice sites as confirmed by EXAFS and DFT data. Enabled by their small ionic size they go off-center, form interacting electric dipoles, and undergo a dipole glass transition at T_ge = 38 K. Subsequently, the Mn2+ spins (S = 5/2) freeze independently into a spin glass at T_gm = 34 K[1]. Both systems show generic glass behavior (divergent relaxation times at T_g, memory and rejuvenation after aging etc.). In addition, they show strong magneto-electric coupling supported by the large optical soft-mode fluctuations in the host crystal, SrTiO_3, which comes close to a ferroelectric instability. The observed symmetry-allowed biquadratic (E ^ 2H ^ 2) coupling is at the origin of the large spin glass temperature, T_gm, which is described within the framework of a transverse Ising model. Analogous experiments on related magnetoelectric quantum paraelectric ceramics K_0.98Mn_0.02TaO_3 (multiglass) and EuTiO_3 (antiferromagnetic) will also be discussed.

[1] V.V. Shvartsman et al, PRL 101 (2008) 165704; W. Kleemann et al, JPCM 20 (2008) 434216

CH-6.6:IL06 **Flexomagnetoelectric Interaction and New Effects in Multiferroics**

A.P. Pyatakov[1, 2]*, A.K. Zvezdin[2], [1]Physics Department, M.V. Lomonosov Moscow State University, Moscow, Russia; [2]A.M. Prokhorov General Physics Institute, Russian Academy of Science, Moscow, Russia

Flexoelectric phenomena relate the electric polarization and flexural deformation that can take the form of cycloid-like spatial modulation of the order parameter (e.g. stripe-like domain patterns induced by electric field in nematic liquid crystals[1]). In magnetic media there is an analogue to flexoelectric energy called inhomogeneous magnetoelectric interaction[2, 3]. This spin flexoelectricity causes various effects: - Improper ferroelectric polarization induced by magnetic ordering in multiferroics and inverse effect: spatially modulated spin structures stabilized by electric polarization; - The pinning of antiferromagnetic domain structure at ferroelectric domain walls as well as spin modulation induced by ferroelectric domains; - The electric field driven magnetic domain wall motion and electrically induced micromagnetic structure transformation; - The minimum in magnon dispersion curve reflecting the instability with respect to the transition to spin modulated state.

[1] Lelidis, G. Barbero, Phys. Lett. A, 311, 242 (2003); [2] V.G. Bar’yakhtar et al, JETP Lett. 37, 673 (1983); [3] A.K. Zvezdin, A.P. Pyatakov, Physics-Uspekhi, 52 (8), 11 (2009)

CH-6.6:IL07 **Local Polarization-dependent Electron Transport through Uni- and Multiaxial Ferroelectric Oxides**

Petro Maksymovych, Arthur P. Baddorf*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA

An ultrathin ferroelectric oxide acting as a tunnel barrier, can exhibit intrinsic switchable and non-volatile conduction states. This prototypical effect is a stepping stone to novel transport phenomena due to soft-phonon order parameters in ferroelectric and multiferroic materials. Ferroelectric tunneling has remained a largely theoretical concept for almost thirty years. Using simultaneous conductive and piezoresponse force microscopy in ultra-high vacuum we have revealed spatially and temporally reproducible polarization control of Fowler-Nordheim electron tunneling into epitaxial Pb(Zr0.2Ti0.8)O3 thin films, manifested as giant enhancement of conductance upon polarization reversal on <20 nm length-scale[1]. Polarization-controlled transport was subsequently found in thin films of multiferroic BiFeO3 (BFO). We will discuss switchable polarization and transport mechanism in BFO films down to 4-5 unit cells, the role of in-plane polarization component, and manipulation of local conductivity of BFO(100) surface by ferroelastic 109deg domain walls. This research at the ORNL’s Center for Nanophase Materials Sciences was sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy.

[1] Maksymovych, Jesse, Yu, Ramesh, Baddorf, Kalinin, Science 324 (2009) 1421

CH-6.6:IL08 **Nonlinear Optics Applied to Magnetoelectric Multiferroics**

Manfred Fiebig, HISKP, University of Bonn, Bonn, Germany

Recently, an enormous interest in multiferroics - compounds uniting two or more forms of primary ferroic ordering in one phase - is observed. From a technological point of view the so-called magnetoelectric cross-correlation between the magnetic and the electric ferroic state is compelling. On the other hand, the interplay of different forms of (anti-) ferroic ordering is a rich source for exploring the fundamental science of phase control. In my talk I discuss the investigation of various multiferroics by optical second harmonic generation (SHG). SHG is a symmetry sensitive technique. Therefore, it allows one to probe the magnetic and the electric order in the same experiment and reveal the interplay of the coexisting ferroic structures. In particular, spatial resolution allows one to image coexisting domain structures and reveal their interaction. I will focus on three fundamentally different multiferroics, namely hexagonal RMnO3 and orthorhombic MnWO4 and TbMn2O5, and discuss their rich variety of magnetoelectric coupling effects, paying particular attention to the formation of multiferroic domains.

CH-6.6:L09 **Photoconductivity in Ferroelectric BiFeO3-PbTiO3 Thin Films**

Xiaowen Zhou*, Shengwen Yu, Bingrong Yuan, Jinrong Cheng, School of Material Science and Engineering, Shanghai, China

We fabricated 7BiFeO3-3PbTiO3 (BFO-PT) thin films on ITO/glass substrate by sol-gel technique. The ITO/glass supported BFO-PT thin film is yellow colored transparent and proved to be reasonable ferroelectric by the hysteresis loops. The dark conductivity of the Pt/BFO-PT/ITO film system was quite low, about $3\cdot10^{-5}$A/cm2. Whereas over one order increased conductivity was observed when the thin film was exposed under visible light source. This could explore the potential application of BFO-PT thin film in optoelectronic device with visible light wavelength. To verify the applicability, the contribution to the photoconductivity in the BFO-PT thin film is studied comprehensively in this work. Various electrode materials and light sources have been adopted in the investigation and the corresponding photoelectrical responses are discussed.

Session CH-6.7
Devices and Applications

CH-6.7:IL01 **Microwave Magnetoelectric Interactions in Composites and Novel Devices**

Y.K. Fetisov*, Moscow State Institute of Radio Engineering, Electronics and Automation, Moscow, Russia; G. Srinivasan, Department of Physics, Oakland University, Rochester, Michigan, USA

A new class of magnetic and electrical field tunable ferrite-piezoelectric microwave devices using magnetoelectric interactions in composite structures has been suggested, designed and characterized[1]. The devices are based on ferromagnetic resonance or magnetostatic wave excitations in thin yttrium-iron-garnet (YIG) or hexaferrite films. Resonators, phase shifters, delay lines and modulators are made of ferrite - lead zirconate titanate (PZT) or lead magnesium niobate - lead titanate (PMN-PT) bilayers in a microstipline structure. The devices provide electrical field control of resonator frequency, phase shift or delay time due to magnetoelectric interactions at the interface of the mechanically coupled piezoelectric and magnetostrictive layers. For an electric field E = 10 kV/cm applied to PZT or PMN-PT, a frequency shift of 30-100 MHz, a phase shift of 0-1350, a 10-25% variation in the delay time, and fast switching of microwave power level are measured for devices operating in the 1-100 GHz frequency band.

[1] G. Srinivasan, Y. Fetisov, Integrated Ferroelectrics, 83, 1 (2006)

CH-6.7:IL02 **Multiferroic Tunnel Junctions: from Theory to Experiment**

Chun-Gang Duan, Key Laboratory of Polar Materials and Devices, East China Normal University, Shanghai, China

Multiferroic Memory is the so called dream device in the field of information science and technology. Here we report a multiferroic tunnel junction (SrRuO3/BaTiO3/SrRuO3) which combines the advantage of magnetic and ferroelectric tunnel junctions. Our first-principles calculations indicate that due to sensitivity of the conductance to both the magnetization alignment of the electrodes (magnetoresistance) and orientation of the polarization in the ferroelectric barrier (electroresistance), this junction can serve as a four-state resistance device, i.e., the resistance of such a multiferroic tunnel junction is significantly changed when the electric polarization of the barrier is reversed and/or when the magnetizations of the electrodes are switched from parallel to antiparallel. These results reveal exciting prospects of multiferroic tunnel junction for application in multifunctional and low energy-cost electronic devices. Also we will talk about the experimental progress in the ferroelectric and multiferroic tunnel junctions.

CH-6.7:IL03 **Tunneling Across a Ferroelectric Barrier: A First-principles Study**

Daniel Bilc[1]*, Frederico D. Novaes[1, 2], Pablo Ordejon[3], Jorge Iñiguez[2], Philippe Ghosez[1], [1]Physique Théorique des Matériaux, Université de Liège, Sart Tilman, Belgium; [2]Institut de Ciència de los Materials de Barcelona-CSIC, Campus de la UAB, Bellaterra, Spain; [3]Centre d'Investigacio en Nanociència i Nanotecnologia -CSIC, Campus de la UAB, Bellaterra, Spain

Ferroelectric tunnel junctions (FTJ), including a ferroelectric as the barrier material, have recently attracted a lot of interest since they are potentially interesting for technological applications such as data storage. In such system, the barrier has to be sufficiently thin to allow for tunneling but must at the same time remain ferroelectric, a property that tends to be suppressed in ultrathin films. The first-principles modeling of FTJ remains challenging mainly because typical density functional calculations within the LDA and GGA significantly underestimate the bandgap of insulators and so produce erroneous Schottky barriers. In a first part, we introduce a new hybrid approach for the correct description of Schottky barrier at metal/ferroelectric interfaces and discuss trends for typical ferroelectrics and metals. In a second part, we consider a prototypical system made of a ferroelectric oxide film between two gold electrodes and compute the I-V curve of the system using density functional theory and Non-Equilibrium Green's Function (NEGF+DFT) formalism. Our atomic-scale approach allows for the first time accurate and self-consistent description of the screening at the metal ferroelectric interface and of the atomic relaxation. It predicts that the asymmetry in the I-V curve for up and down polarizations is sufficiently large to be detected experimentally at finite bias even for symmetric FTJ. This opens the door to applications in which the tunneling current allows the reading of the polarization state. Work supported by the European project OxIDes and the EMMI.

CH-6.7:IL04 **Sub-THz Excitations in Ferrite-ferroelectric Heterostructures**

G. Srinivasan, Physics Department, Oakland University, Rochester, MI, USA

There has been interest in recent years in pure and substituted hexaferrite films as a promising material for Sub-THz devics. This presentation will focus on magnetic and dielectric resonances in the hexaferrites over 50-110 GHz, magneto-electric (ME) interactions in a bilayer with piezoelectrics, and tuning of the modes with electric and/or magnetic fields. It is known that the substitution for iron (Fe3+) in M-type hexaferrite by aluminum (Al3+) allows to increase significantly the uniaxial magnetocrystalline anisotropy field and, consequently, to achieve ferromagnetic resonance (FMR) frequencies of 100 GHz or more for reasonable values of bias magnetic fields. When the ferrite is bonded to a piezoelectric, one has the additional capability to tune the resonances with an electric field applied to the piezoelectric. It is also possible to excite dielectric resonance in the ferrites in the sub-THz region with proper choice for the sample dimensions and tune their frequencies with a magnetic field. Resonators of single-crystal aluminum substituted barium hexaferrites with polycrystallin PZT or single crystal PMN-PT were studied. Results indicate strong ME interactions and potential use of the composites for sub-THz filters and phase shifters.

CH-6.7:IL05 **Taking Advantage of Interface Effects to Design New Oxide Based Heterostructures for Spintronics**

A. Barthélémy[1]*, M. Bibes[1], Z. Sefrioui[3], V. Garcia[1, 2], O. Copie[1], M. Basletic[5], K. Bouzehouane[1], S. Fusil[1], E. Jacquet[1], D. Imhoff[4], L. Bocher[4], A. Hamzic[5], J. Santamaria[3], N. Mathur[2], [1]Unité Mixte de Physique CNRS/Thales, Palaiseau, France; [2]University of Cambridge, Cambridge, UK; [3]GFMC, Dpto. Fisica Aplicada III, Universidad Complutense de Madrid, Spain; [4]Lab. de Physique des Solides, CNRS, Université Paris-Sud, Orsay, France; [5]Dept. of Physics, University of Zagreb, Zagreb, Croatia

Due to the large diversity of their physical properties the role of oxides in spintronics has continuously increased[1]. To illustrate our work in this field, I will present results on all manganite tunnel junctions in which ferromagnetism is induced in the barrier by proximity effect resulting in a spin filtering phenomena[2]. I will present experiments on heterostructures combining ferroelectric tunnel barriers of BaTiO3 and ferromagnetic electrodes and the consequent tunnel magnetoresistance (TMR) and tunnel electroresistance (TER)[3]. They also exhibit an interfacial magnetoelectric coupling that results in a modulation of the spin polarisation at the interface by the ferroelectricity resulting in a TEMR (Tunnel Electro MagnetoResistance) effect[4]. I will also present results on the conduction at the interface between two insulating materials SrTiO3 and LaAlO3 and the experiments performed in order to determine the extension of this electron gas[5].

[1] Bibes and Barthélémy; IEEE Trans. Electron Dev. 54, 1003 (2007); [2] Sefrioui et al, to be published; [3] Duan et al, PRL 97, 047201 (2006); Fechner et al, PRB 78, 212406 (2008); [4] Garcia et al, Nature 460, 81 (2009); [5] Basletic et al, Nat. Mat. 7, 621 (2008); Copie et al, PRL 102, 216804 (2009)

CH-6.7:IL06 **Ferroelectric Tunnel Barriers for Electronics and Spintronics**

M. Bibes, Unité Mixte de Physique CNRS/Thales, Palaiseau, France

Ferroelectrics possess a polarization that is spontaneous, stable and electrically switchable, providing a way to store a non-volatile information that can be written and read by purely electrical means. Junctions based on nanometer-thick ferroelectric tunnel barrier were devised as early as 1971 as potential novel memories showing electroresistance effects, but have remain elusive until recently due to challenges in stabilizing ferroelectricity at very low thickness. In this talk, I will show that strain-engineered 1 to 3 nm-thick BaTiO3 films can be ferroelectric at room temperature. When used as tunnel barriers, they provide a giant modulation of the tunnel current by the direction of ferroelectric polarization, with electroresistance on/off ratios close to 1000 [Nature 460, 81 (2009)]. While this effect can be understood in terms of the influence of ferroelectricity on the tunnel transmission coefficient, a substantial impact on the density of states at interfaces between the barrier and the electrodes is also expected. With ferromagnetic electrodes, this latter mechanism provide the unique opportunity to control electrically and in a non-volatile manner the spin polarization of the tunnel current. Results on such artificial multiferroic tunnel structures will be presented.

Poster Presentations

CH-6:P02 **Microstructure, Magnetic and Dielectric Properties of $CoFe_2O_4$-Pb($Fe_{1/2}Ta_{1/2}$)O_3-$PbTiO_3$ Composites**

J. Kulawik*, P. Guzdek, D. Szwagierczak, Institute of Electron Technology, Cracow Division, Kraków, Poland

Combination of ferromagnetic and ferroelectric materials is a typical way to achieve multiferroic properties. This paper reports on composite ceramics based on cobalt ferrite and lead iron tantalate relaxor, which is a single phase multiferroic. Syntheses of $CoFe_2O_4$ (CF) and Pb($Fe_{1/2}Ta_{1/2}$)O_3 (PFT) were performed by conventional solid state reactions. $PbTiO_3$ (PT) was introduced to shift upwards the ferroelectric transition temperature. 0.5CF-0.425PFT-0.075PT bulk composites were prepared by sintering at 900 °C. X-ray diffraction analysis and scanning electron microscopic observations confirm that the obtained ceramic samples are composed of ferrite spinel and relaxor perovskite phases. Impedance spectroscopic studies carried out in the temperature range from -55 to 500 °C at frequencies 10 Hz-2 MHz show high and broad maxima of dielectric permittivity, reaching 5000 at 1 kHz. On the basis of investigations of magnetization versus magnetic field (up to 85 kOe) and temperature (from -269 to 127 °C), the behavior typical of hard magnetic materials was found for CF-PFT-PT ceramics. The measurements carried out as a function of the external static magnetic field and frequency of the sinusoidal modulation field, reveal a distinct magnetoelectric effect of the investigated composites.

CH-6:P03 **The Ferroelectric and Optical Properties of $BiFeO_3$-$PbTiO_3$/ZnO:Al Heterostructure**

W.F. Yang*, S.W. Yu, J.R. Cheng, School of Materials Science and Engineering, Shanghai University, Shanghai, China

$BiFeO_3$-based thin films are well known for their multiferroelectric features. In this work, we prepared the heterostructure of $BiFeO_3$-$PbTiO_3$/ZnO:Al on transparent optical substrates by the sol-gel method. The conductive Al doped ZnO layer (ZnO:Al) works not only as a component in the heterosturcutre but also as the bottom electrode during the electrical measurements. With this integrated structure, novel ferroelectric and optical properties could be expected. XRD and SEM are characterized to check the microstructure and morphologies of the film system to reveal the synthesis information. Electrical (dielectric, ferroelectric and leakage current), optical (UV-vis absorption) properties and photo-current are carefully inspected to elucidate the capability of this heterostructured film as a potential material in optoelectronic devices.

CH-6:P04 **Synthesis of Some Aurivillius Phases in the Bi-Fe-Ti-O System by Wet Chemical Methods**

Dariusz Zientara*, Miroslaw M. Bucko, Joanna Polna,r AGH - University of Science and Technology, Faculty of Materials Science and Ceramics, Cracow, Poland

The Aurivillius phases in the Bi-Fe-Ti-O system showing multiferroic properties arouse an increasing interest due to their wide potential applications in electronics. These compounds were usually prepared by high temperature solid-state reaction method using respective oxide powders mixed in required stoichiometry. An excess of bismuth oxide was often added due to its evaporation during heat treatment. The mixture of the oxide powders were calcined in air between 700 and 900 °C for several or even for several dozen hours. To achieve dense polycrystalline bodies sintering of such powders was usually performed at 1000 °C. In the present paper some Aurivillius phases were prepared by wet chemical methods. Co-precipitation of respective oxides and hydroxides with ammonia in different variants was used. The co-precipitated gels were calcined at different temperatures and X-ray diffraction analysis was used for identification of phase composition of the products. It was stated that temperature of synthesis of the pure Aurivillius phase depended on the way co-precipitation.

CH-6:P05 **$Eu_{0.5}Ba_{0.5}TiO_3$ - A New Magnetoelectric Multiferroics**

V. Goian*, S. Kamba, P. Vanek, M. Savinov, D. Nuzhnyy, K. Knizek, Institute of Physics ASCR, Prague, Czech Republic; J. Prokleska, Charles University, Prague, Czech Republic

Solid solution of antiferromagnetic quantum paraelectric $EuTiO_3$ (TN = 5.3 K) and ferroelectric $BaTiO_3$ (Tc = 390 K) was prepared. $Eu_{0.5}Ba_{0.5}TiO_3$ ceramics were sintered at 1300 °C for 24 hr in Ar+10%H_2 atmosphere. The samples exhibited a ferroelectric phase transition from cubic to tetragonal phase near 240 K and a magnetic phase transition at 1.9 K. Infrared and THz spectra revealed ferroelectric soft mode in the paraelectric phase and its splitting in the ferroelectric phase. This confirmed a displacive character of the phase transition. Superexchange interaction is responsible for antiferromagnetic ordering in $EuTiO_3$, but this interaction is remarkably reduced due to Ba doping in Eu sites and therefore a spin glass behavior was observed at low temperatures. The value and origin of magnetoelectric coupling in $Eu_{0.5}Ba_{0.5}TiO_3$ will be discussed.

CH-6:P06 **Magnetic Properties of Some Aurivillius Phases in the Bi-Fe-Ti-O System**

Miroslaw M. Bucko, Czeslaw Kapusta AGH - University of Science and Technology, Faculty of Materials Science and Ceramics, Cracow, Poland

Multiferroic materials, have received much interest because of their possible applications including electrically controlled microwave devices, ferromagnetic resonance devices, magnetically controlled electro-optic, broadband magnetic field sensors, and ME memory devices. The multiferroic Aurivillius phases in the Bi-Fe-Ti-O system are built from alternate (Bi_2O_2)2+ and ($Bi_{n-1}X_nO_{3n+1}$)2? layers, where X = Fe3+, Ti4+ and "n" refers to the number of perovskite-like layers between Bi_2O_2 layers Detailed magnetic studies should be done to understand electromagnetic interactions and multiferroic coupling effects. In the present paper powders of the Aurivillius phases with n = 5, 6 and 7 were prepared by wet chemical method. The powders were sintered to dense polycrystalline materials. Field cooled - zero field cooled dc magnetization measurements were performed in the temperature range of 4-300 K using a 9 T vibrating sample magnetometer. It was stated that magnetic properties of the samples and temperatures of magnetic phase transformation are depend on structure of the respective Aurivillius phases.

CH-6:P07 **Effects of Magnetic Ordering on Ferroelectric Polarization Switching Behavior of $YMnO_3$ Epitaxial Thin Film**

Kazuhiro Maeda*, Takeshi Yoshimura, Norifumi Fujimura, Graduate School of Engineering, Osaka Prefecture University, Osaka, Japan

The switching behavior of ferroelectric polarization of magnetic ferroelectric (0001) $YMnO_3$ epitaxial film at around the Néel temperature (= 80K) was investigated to discuss the effect of antiferromagnetic ordering on ferroelectric polarization behavior. The temperature dependences of polarization-electric field and capacitance-voltage characteristics were measured in the temperature range from 300 to 10 K. Anomalies such as increase of the spontaneous polarization and decrease of the dielectric permittivity under electric filed are observed at 80 K, which indicates magnetoelectric coupling. From results to investigate temperature dependence of ferroelectric domain wall motion and density, enhancement of sidewise domain growth, increase of domain size and velocity of domain wall motion with decreasing temperature is revealed. Moreover, it was found that polarization switching is suppressed at around 120-130 K, which is higher than Néel temperature of $YMnO_3$. At around 130 K, spin-phonon coupling are recognized using Raman scattering measurement. It suggests that effects of magnetic order on ferroelectric polarization switching.

Symposium CI

MAGNETIC AND TRANSPORT PROPERTIES OF OXIDES

Oral Presentations

Session CI-1
CMR Manganites

CI-1:IL01 **Emergent Phenomena in Complex Oxides under Spatial Confinement**
T.Z. Ward[1]*, Jian Shen[1, 2], [1]Materials Sciences and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA; [2]Dept. of Physics, Fudan University, Shanghai, China

For condensed matter physicists, materials are often separated into two classes: simple materials and strongly correlated materials. Because the interested problems are very different, there is, traditionally, very little overlap between the two fields. However, in the world of reduced dimensionality, the line is no longer well defined. Simple materials can become complex, and complex materials can become even more complex, or, sometimes, simple. In this talk, I will use a complex material La5/8-xPrxCa3/8MnO3 (LPCMO) to demonstrate how emergent phenomena appear in reduced dimensionality. The emergent phenomena mostly originate from the electronic phase separations (EPS) in the LPCMO system. Helped by spatial confinement, the nature of the EPS including their dynamics can be cleanly studied using conventional transport measurements. It is hoped that these work will lead to a new field where the interplay between complexity and quantum effect will generate fascinating new properties for future technology.

CI-1:IL02 **Bilayer Manganites: Neutron Scattering Studies**
Tapan Chatterji, JCNS, FZ Juelich outstation at Institut Laue-Langevin, Grenoble Cedex, France

I shall review the results of our neutron scattering investigation on the optimally doped quasi-two-dimensional bilayer manganite La1.2Sr1.8Mn2O7 that shows colossal magnetoresistance (CMR) behaviour and compare them with those obtained in three-dimensional CMR manganites. The reduced dimensionality plays a central role in the magnetic and CMR properties of the bilayer manganites by enhancing the CMR effect albeit at the cost of reduced ferromagnetic transition temperature Tc. We have studied the spin dynamics of La1.2Sr1.8Mn2O7 by inelastic scattering and modeled it first by a simple Heisenberg Hamiltonian to get a complete set of exchange interactions. However, this simple model fails to explain the damping and zone-boundary softening observed even at low temperatures. A quantum theory of spin dynamics based on minimal double-exchange model that reproduced qualitatively the spin wave damping and zone-boundary softening has been developed. We observed persistent spin waves above Tc expected for a quasi-two-dimensional magnetic system. The dynamical structure function and the spin autocorrelation function have been calculated both below and above Tc using Monte-Carlo molecular-dynamics technique and have been compared with the the experimental results.

CI-1:IL03 **Charge Ordering and Related Phenomena of Manganites on Nano-scale**
Indranil Das, Saha Institute of Nuclear Physics, Experimental Condensed Matter Physics Division, Kolkata, India

I will be discussing some of our novel findings in the field of manganite nanoparticles. In the literature little attention has been paid towards nanocrystalline form of manganites. The main objective of our study is to investigate the modification of charge ordering and related phenomena in manganites due to the reduction of particle size. We have observed the disappearance of charge order transition (COT) in the cases of nanocrystalline Pr0.5Sr0.5MnO3 and Nd0.5Sr0.5MnO3. However, COT in nanoparticle is observed for the first time in Pr0.65Ca0.35MnO3 of particle size ~40 nm. Our studies suggest that the martensitic-like character of COT is the primary factor for stabilization of charge ordered state (COS) in nanoparticles. The co-existence of COS and ferromagnetic state can have strong influence on the magnetotransport and magnetocaloric properties of nanocrystalline Pr0.65(Ca1-ySry)0.35MnO3. In contrast to the general believe the systems exhibit large LFMR [and magnetocaloric effect (MCE)] due to the destabilization of charge ordered state by magnetic field. Our recent experimental observation indicates that the nanocrystalline La0.125Ca0.875MnO3 exhibits giant inverse MCE below antiferromagnetic transition due to the inhomogeneous exchange interaction at the phase boundary.

CI-1:IL04 **Interface Magnetism in Complex Oxide Heterostructures and Nanostructures**
Hariharan Srikanth, Department of Physics, University of South Florida, Tampa, FL, USA

Magnetic oxides are an important class of materials from the perspectives of fundamental physics and technological applications. Advances in growth of high quality thin films and nanostructures over the years, have led to the realization of ideal condensed matter systems in which the complex and rich physics associated with cooperative phenomena can be explored. Examples of coupled phenomena in complex oxides include exchange bias effects, charge and orbital ordering, interplay between magnetism and superconductivity. In this talk, I will focus on three classes of oxides –multiferroic LuFe2O4, bulk and nanostructured mixed-phase manganite (La,Pr,Ca)MnO3 and high-pressure sputtered LCMO/YBCO films. The common theme is the coupled effects across intrinsic and extrinsic interfaces. I will demonstrate that relatively unconventional experiments such as dynamic transverse susceptibility and magnetocaloric effect (MCE) are effective probes of cooperative phenomena involving structure, magnetic, electronic coupling in complex oxides. In the case of LuFe2O4, I will elucidate the origin of multiple magnetic transitions arising from cluster glass phases. Competing and co-existing charge order and ferromagnetic phases in mixed phase manganites and the influence of nanostructuring on magnetic properties will be discussed. Lastly, I will present evidence for direct coupling between the magnetic moments in LCMO and the vortex lattice in YBCO in LCMO/YBCO heterostructures.

Research supported by the US Department of Energy and the Army Research Office.

CI-1:IL05 **Many Faces of Photoinduced Phases in CMR Manganites**
Kenjiro Miyano, RCAST, University of Tokyo, Tokyo, Japan

In view of the recent surge of interest in the multiferroic aspect in CMR manganites, it is appropriate to review how photoexcitation, basically a single particle process acting only in the charge sector, can modify the overall electronic properties including magnetism. Quite naively, one can presume that the excited states are more extended and hence the photoinduced phase is metallic and ferromagnetic due to double exchange effect. Therefore, in the early days, the photoinduced insulator to metal transition was vigorously searched for[1]. Later, however, it became clear that there are many more varieties in the photoinduced effects, including the metal to insulator transition[2], no transition[3], and transition into a non-thermal state[4]. Although in retrospect it is obvious, the varying behavior depends on the delicate balance of many degrees of freedom, the lattice being one important player. I will go over some of these examples.

[1]K. Miyano et al, PRL 78, 4257 (1997); [2]N. Takubo et al, PRL 101, 177403 (2008); [3]H.Tamaru et al, PRB 78, 075119 (2008); [4]Ichikawa et al, in preparation

CI-1:L06 **Self-adaptative Composition Modulation in Strained Manganite Thin Films**
J. Fontcuberta, I.C. Infante, F. Sanchez, Institut de Ciencia de Materials de Barcelona - CSIC, Bellaterra, CAT, Spain; S. Estrade, J. Arbiol, F. Peirò*, EME/CeRMAE/IN2UB, Dept. d'Electronica, Universitat de Barcelona, Barcelona, CAT, Spain; F. de la Pena, M. Walls, C. Colliex, Laboratoire de Physique des Solides, (UMR CNRS 8502), Batiment 510, Universite Paris Sud, Orsay, France; M. Wojcik, E. Jedryka , Institute of Physics, Polish Academy of Sciences, Warszawa, Poland

Interfaces in epitaxial heterostructures of oxides are receiving much interest due to the emerging properties observed. Detailed understanding is hampered by the absence of detailed knowledge of the chemistry and atomic structure of interfaces. Here, we take advantage of the extreme sensitivity of the properties of La1-xCaxMnO3 to minute changes on composition, to monitor substrate-induced strain effects. Electron-Energy-Loss Spectroscopy is used to map composition and electronic states in La2/3Ca1/3MnO3 films of various thicknesses grown on SrTiO3 (001) and (110) substrates. For relatively thick films, epitaxial tensile strain in (001)films promotes a compositional La/Ca gradient across the film thickness, being the interface La rich,while the relaxed(110) films are chemically homogeneous. Much thinner films display a different La/Ca d istribution being La rich at the free surface. X-rays and NMR are used to monitor structural and atomic changes. Our observations suggest that a strongly orientation-dependent self-adaptative composition mechanism dominates stress accommodation and provides understanding of their magnetic properties. The observed distinct thickness-dependent composition gradient behaviour could reflect a balance between elastic energy kinetic effects during growth.

Session CI-2
Multiferroic Compounds

CI-2:IL01 Room-temperature Multiferroic Coupling of BiFeO3

Je-Geun Park, Department of Physics & Astronomy, Seoul National University, Seoul, Korea

Multiferroics, or materials displaying the coexistence of ferroelectricity and magnetism, is rare in nature. However, coupling between both order parameters is the subject of fundamental physical interest and has immense potential for industrial applications. Among the known multiferroics BiFeO3 is arguably the most studied compound and, more importantly, the only material with both transitions above room temperature, simultaneously having a large polarization of 86 ìC/cm2. For nearly half a century, however the physical mechanism leading to the coexistence of both phases and to their coupling in BiFeO3 remains unanswered. By performing high resolution synchrotron and neutron diffraction studies on high quality single crystals, we have addressed this long standing puzzle and show how the coupling occurs at an atomic level. We argue that the exceedingly large non-volume conserving magnetoelastic effect observed by us, combined with an incommensurate magnetic order, is the key necessary ingredient for the coupling between magnetization and polarization in this system.

This work was carried out under collaboration with J. Park, S-H. Lee, S. Lee, F. Gozzo, H. Kimura, Y. Noda, Y.J. Choi, V. Kiryukhin, S-W. Cheong, Y.J. Jo, E.S. Choi, L. Balicas, and G.S. Jeon.

CI-2:IL02 Exotic Ferroelectricity Induced by Spin or Charge Order

S. Picozzi, CNR-INFM, CASTI Regional Lab., L'Aquila, Italy

Electronic magnetic ferroelectrics, i.e. complex magnetic oxides in which ferroelectricity is driven by non-centrosymmetric spin- or charge- or orbital-arrangements, have recently attracted great interests. By means of density functional studies, we will focus on the existence and efficiency of different mechanisms for multiferroicity (i.e. coexistence of long-range dipolar and magnetic orders), based on the interplay between electronic and structural degrees of freedom[1]. In closer detail, we will present cases (HoMnO3, nickelates[2] or sulfides), in which the electric polarization is magnetically induced. Furthermore, we will show the paradigmatic case of magnetite, in which ferroelectricity is induced by a non-centrosymmetric charge-order of Fe2+/Fe3+ on Fe B sites.[3] Finally, we will present promising avenues towards other examples where charge-ordering or spin-ordering or a combination of both spin-and-charge-ordering driven ferroelectricity can occur, in terms of novel materals, unconventional mechanisms and related efficiency.

[1]For further info, see http://www.casti.aquila.infn.it/homepages/bismuth/index.html; [2]Giovannetti G et al, 2009 Phys. Rev. Lett.. 103, 156401; [3]Alexe M et al, 2009 Adv. Mater. 21, 1

CI-2:IL03 Electronic Orbital Currents and Polarization in Mott Insulators

D. Khomskii, II. Physikalisches Institut, Universitaet zu Koeln, Koeln, Germany

The standard point of view is that at low energies Mott insulators exhibit only magnetic properties, while charge degrees of freedom are frozen out, because electrons are localized. We demonstrate that in general this is not true[1]: for certain spin textures there exist quite nontrivial effects in the ground and lowest excited states, connected with charge degrees of freedom. We show that in some cases there may exist spontaneous circular currents in the ground state of insulators, proportional to the scalar chirality. For other spin structures there may exist spontaneous charge redistribution, so that average charge at a site may be different from 1. This can lead to the appearance of dipole moments and possibly of the net spontaneous polarization. This is a novel, purely electronic mechanism of multiferroic behaviour. We discuss also some dynamic consequences of the effects discovered, such as dipole-active "ESR" transitions, rotation of electric polarization by magnetic field and the appearance of negative refraction. The possibility to use chirality as qubits will be also discussed.

[1]L.N. Bulaevskii, C.D. Batista, M.V. Mostovoy and D.I. Khomskii, "Electronic Orbital Currents and Polarization in Mott Insulators", Phys.Rev.B 78, 028402 (2008)

CI-2:IL04 Strain Engineered Magnetoelectric Coupling and Ferroelectricity in Orthorhombic AMnO3 Epitaxial Thin Films

J. Fontcuberta*, X. Marti, I. Fina, L. Fabrega, F. Sanchez, Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra, Spain; V. Skumryev, Universitat Autonoma de Barcelona (UAB), Dept. Fisica, Campus UAB, Bellaterra, Spain and Institut Catala de Recerca i Estudis Avancats, Barcelona, Spain; C. Ferrater, M. Varela, Universitat de Barcelona, Dept. Fisica Aplicada i Optica, Barcelona, Spain

Orthorhombic perovskites o-AMnO3 are antiferromagnetic below the Néel temperature (TN~40 K). Here we will report on the growth and characterization of a series of o-AMnO3 films in which the structure is gradually modified via epitaxial strain. We will show that films are basically antiferromagnets at 40 K, and display a pronounced dielectric anomaly at T<TN. Films display hysteresis in their zero-field cooled field-cooled magnetization curves, which indicates the existence of a remnant magnetization (Mr). From the systematic study of the relationship between magnetic and dielectric properties we conclude that: (1) Strain allows to modulate the remanence Mr of the films. (2) The low-temperature dielectric constant changes with the magnetic field thus suggesting magnetoelectric coupling(ME.(3) Polarization emerges abruptly at about 27 K, thus indicating that o-YMnO3 is ferroelectric. In short, we show than the complex magnetic order established in these oxides, below TN, is accompanied by a profound dielectric anomaly that signals ME couplingThe dielectric anomaly, ultimately giving rise to ferroelectricity, and the ME coupling can be subsequently tuned by strain. The origin of ferroelectricity will be discussed.

CI-2:IL06 Charge-based Magnetoelectric Coupling in Complex Oxide Heterostructures

Charles Ahn, Yale University, New Haven, CT, USA

The doped lanthanum manganites are strongly correlated complex oxides exhibiting a strong interplay between charge, spin, and lattice effects. This coupling leads to a variety of electronic behavior, including magnetic and charge ordered states, "colossal" magnetoresistance (CMR), and a range of electron transport behavior. The possibility of using this multifunctional behavior has been a driving force in the development of new oxide-based materials systems exhibiting novel physical properties, including multiferroic composite heterostructures. In this talk, we present results demonstrating a large charge-driven, magnetoelectric coupling in $La_{1-x}Sr_xMnO_3/PbZr_xTi_{1-x}O_3$ multiferroic heterostructures. Epitaxial films have been grown by r.f. magnetron sputtering and molecular beam epitaxy on $SrTiO_3$(001) substrates. Measurements of the magnetization as a function of the temperature and applied electric field using magnetooptic Kerr effect magnetometry show a large change in the magnetic critical temperature and magnetic moment of the $La_{1-x}Sr_xMnO_3$ layer for the two polarization states of the PZT layer, which modulates the charge-carrier concentration at the $La_{1-x}Sr_xMnO_3$ interface. This magnetoelectric coupling is purely electronic in origin, which is attributed to changes in the Mn valency and to the presence of competing ground states in the CMR manganites. We have observed this change in the Mn valency directly by studying the electronic state of the Mn cations using near-edge x-ray absorption spectroscopy. The large magnetoelectric effect demonstrated here is a consequence of the sensitivity of the electronic states of these materials to charge, a hallmark of this class of strongly correlated metal oxide systems. We also consider the integration of these systems onto a silicon platform.

Session CI-3
Magnetic Oxide Thin Films and Heterostructures

CI-3:IL01 **Tuning the Electronic Properties of the LaAlO3/SrTiO3 Interface**

A. Caviglia[1], N. Reyren[1], S. Gariglio[1], C. Cancellieri[1], S. Thiel[2], G. Hammerl[2], D. Jaccard[1], M. Gabay[3], T. Schneider[4], J. Mannhart[2], J.-M. Triscone[1]*, [1]DPMC, University of Geneva, Geneva, Switzerland; [2]Experimental Physics VI, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, Augsburg, Germany; [3]Laboratoire de Physique des Solides, Université d'Orsay, Orsay, France; [4]Physik Institut, University of Zurich, Zurich, Switzerland

At interfaces between complex oxides, electronic systems with unusual properties can be generated[1]. A striking example is the interface between LaAlO3 and SrTiO3, two good insulating perovskite oxides, which was found in 2004 to be conducting with a high mobility[2]. We discovered that the ground state of this system is a superconducting condensate, with a critical temperature of about 200 mK[3]. The characteristics observed for the superconducting transitions are consistent with a two-dimensional superconducting sheet as thin as a few nanometers. Recent field effect experiments revealed the sensitivity of the normal and superconducting states to the carrier density[4]. In particular, the electric field allows the tuning of the critical temperature between 200 mK and 0 K and thus the on-off switching of superconductivity, revealing a complex phase diagram and a superconductor to insulator transition. Recent results reveal a large tunable spin-orbit coupling and a remarkable correlation between the spin-orbit coupling strength and the system phase diagram.

[1]See for instance, J. Heber, Nature 459, 28 (2009); [2]A. Ohtomo, H.Y. Hwang, Nature 427, 423 (2004); [3]N. Reyren et al, Science 317, 1196 (2007); [3]A. Caviglia et al, Nature 456, 624 (2008)

CI-3:IL02 **Magnetotransport and Magnetic Properties of All Oxide Magnetic Multilayers**

N. Keller[1]*, B. Berini[1], J. Scola[1], W. Noun[1], A. Fouchet[1], E. Popova[1], D. Schmool[2], I. Sheikin[3], A. Demuir[3], P. Lejay[4], [1]GEMaC / CNRS - UVSQ, Versailles, France; [2]IFIMUP, Universitat do Porto, Porto, Portugal; [3]LNCMI, CNRS, Grenoble, France; [4]Institut Néel, Grenoble, France

This study focuses on the magnetic and transport properties of an all oxide heterostructure composed of two magnetic SmFeO3(SFO) layers coupled via a metallic LaNiO3(LNO) layer. Multilayers of [SFO/LNO/SFO] have been grown by laser MBE. Transport properties were investigated from 15 - 300 K for a sample series with varying LNO interlayer thickness of td = 2 - 30 nm. A strong enhancement of the low temperature resistance for td above 4 nm is observed suggesting an antiparallel alignment of the two SFO magnetizations. The magnetic properties of single layers and a single crystal were investigated on another orthoferrite YFeO3(YFO). YFO is a canted antiferromagnet (AFM) whose static order is determined by the perturbation of the AFM due to the Dzyaloshinsky-Moriya interaction (DM). We show that the DM interaction is fully preserved in YFO films as compared to a single crystal. Also a strong irreversibility of the magnetization clearly shows that interdomain coupling intervenes within the layers. In perpendicular field, the magnetization is also orthogonal to the plane and the film exhibits a ferromagnetic-like behavior with a coercitive field of about 3 T. Such high coercitive field makes YFO and SFO films very attractive candidates for exchange biasing in magnetic multilayers.

CI-3:L03 **Measurement of the Transport Spin Polarization of Ru Doped CrO2 Using Point-contact Andreev Reflection**

M.S. Osofsky*, Naval Research Laboratory, Washington, DC, USA; K. West, S.A. Wolf, J. Lu, University of Virginia, Charlottesville, VA, USA

Point contact Andreev reflection (PCAR) has proven to be a versatile tool for evaluating the transport spin polarization of ferromagnetic materials for spintronics applications. I will review the principles behind PCAR and results from a variety of materials that verify its usefulness. It now well known that CrO2 is 100% spin polarized but very difficult to grow in thin film form. We recently demonstrated that high quality films of Ru doped CrO2 can be grown using reactive bias ion beam deposition. Some of these films have Curie temperatures above room temperature and exhibit unusual magnetic behavior including an intrinsic tunable exchange bias. PCAR results on these films will be presented that show that these films are also highly spin polarized compared to conventional metals like Fe.

CI-3:L04 **Effects of Substrate Electrostriction on Thin Films of La0.67Ca0.33MnO3, a Manganite Prone to Phase Segregation**

F.J. Mompean*, A. Alberca, R. Villanueva, N. Biskup, A. de Andrés, M. García-Hernández, ICMM/CSIC Madrid; Norbert M. Nemes, F. Bruno, J. Santamaría, Universidad Complutense de Madrid, Spain

In the bulk phase, La0.67Ca0.33MnO3 (LCMO) exhibits a stronger tendency towards disorder-induced phase segregation and a better defined metal-insulator transition than La0.67Sr0.33MnO3. However, strain in thin films of the latter material can be modeled within cubic symmetry and they have been more extensively studied to demonstrate substrate induced strain effects on magnetic and magnetoresistive properties. We study the magnetic and magnetoresistive response of thin films (5 - 20 nm) of LCMO grown epitaxially on single crystals of two ferroelectrics: BaTiO3 and Pb(Mg0.33Nb0.67)0.72Ti0.28O3 paying attention to the effects of the ferroelectric domain map and the strain induced by the substrate electrostrictive response. Work supported by Spanish MICINN.

CI-3:L05 **Role of Defects and Interfaces in Ferromagnetism of SnO2 Based Heterostructures**

A. Espinosa[1]*, M. García-Hernández[1], N. Menéndez[2], C. Prieto[1], A. de Andrés[1], [1]Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, Madrid, Spain; [2]Departamento de Química-Física Aplicada, Universidad Autónoma de Madrid, Cantoblanco, Madrid, Spain

Several series of A/SnO2 and Mn/B multilayers, where A and B are thin layers (0.4 nm to 10 nm) of SnO2, SiO2, Si, Al, Mn or MnOx, have been grown by sputtering techniques and characterized by a structural, electronic and magnetic study. The observed room temperature ferromagnetic (RTFM) signal does not scale to Mn content but increases with the number of interfaces and their roughness. The presence of Mn in 3+ oxidation state in the SnO2 lattice is a necessary condition but is not enough to promote ferromagnetism which also requires the presence of Sn2+. The high oxygen deficiency induced by Mn doping in the tin oxide layers is compensated by the formation of the stable SnO phase. Moreover, the RTFM signal decreases upon annealing either in O2 rich or in vacuum atmospheres, therefore oxygen vacancies do not seem to play a fundamental role. The combination of Mn with SiO2, Si or Al produces paramagnetic signals but no ferromagnetism; consequently SnO2 is a crucial ingredient of this RTFM.

CI-3:IL06 **Tunable Interfaces in Manganite Multilayers**

Christos Panagopoulos*, Nanyang Technological University, Singapore, and University of Crete, Crete

When two isostructural but chemically distinct materials are put into epitaxial contact, unique phenomena emerge at the interface. One of the most dramatic examples is the formation of a two-dimensional high-mobility electron gas at the interface of two non-magnetic perovskite insulators, such as SrTiO3 and LaAlO3, which at low enough temperature can become ferromagnetic (FM). This discovery may lead to exciting applications, for instance, a novel field effect transistor (FET). While FET is a purely electronic device, epitaxial heterostructures can also provide a basis for novel spintronic devices. For that, at least one of the materials comprising the structure has to be magnetic. For example, it has been recently demonstrated that when put into contact with FM SrRuO3, the boundary (interface) layer of antiferromagnetic (AF) manganite SrMnO3 becomes FM. By performing a systematic study, here we find that the direction of the interface FM can be controlled by the substrate-introduced strain and its magnitude by the chemical composition of the manganite layer of choice. The demonstrated high tunability of magnetic properties on the few unit cell level, may naturally lead to tailor made ultra-miniature oxide-based spintronic devices.

CI-3:IL07 **Phase Transitions in Narrow Band Manganite Thin Films**

U. Scotti di Uccio[1]*, L. Aruta, C. Barone, C. Cantoni, A. Galdi, A. Geddo Lehmann, F. Congiu, N. Lampis, L. Maritato, F. Miletto Granozio, S. Pagano, P. Perna, M. Radovic, [1]CNR-INFM, Complesso Monte S. Angelo, Napoli, Italy

The narrow band manganites host a rich variety of phases with different structure, magnetic ordering, transport properties. The applied fields, including magnetic, electric, stress, etc. may affect in a dramatic way the physical properties, as in the colossal magnetoresistance or electroresistive effects, or giant magnetostriction, etc. In this talk the attention will be mainly concentrated on Pr1-xCaxMnO3, a compound that represents an outstanding example of the complexity of high correlated manganites. A set of experimental results concerning epitaxial films deposited on different substrates will be presented, with the aim of contributing to add some information on the magnetic and transport properties in the different observed phases, with particular reference to the ferromagnetic-insulating FMI and to the charge (orbital) ordered CO (OO) phase, as influenced by the biaxial stress due to the substrate. The talk will regard the magnetic and the electrical transport properties of ultrathin films. Main topics will be: 1) the crossover from the cluster-glass behaviour, similar to bulk, to robust ferromagnetism, in films that are subject to different strain; 2) the nonlinearities in the I-V characteristic and the broadband 1/f noise properties in the charge ordered phase.

CI-3:IL08 **Multichannel Transport of a Two-dimensional Electron Gas at the Interface in Oxide Superlattices**

J.S. Kim, S.S.A. Seo, R.K. Kremer, H.-U. Habermeier, B. Keimer, Ho Nyung Lee*, Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA; Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

In this talk, we report the transport properties of a two-dimensional electron gas formed at the electronically-reconstructed interface in atomic-scale superlattice crystals comprised of unit-cell-thin $LaTiO_3$ layers epitaxially embedded in a $SrTiO_3$ matrix. We find that the magnetic field dependence of the Hall resistivity shows a strong nonlinearity which is significantly modified upon varying the temperature and the electric field. It is very temptating to conclude the behavior as an anormalous Hall effect, our systematic investigation attributes such an anomalous interfacial behavior to a multichannel conduction; i.e. an additional type of charge carriers with very high mobility is generated away from the delta-doped interfaces by the greatly increased screening of the ionic scattering in $SrTiO_3$. In addition, the spatial distribution of such high mobility carriers formed in oxide heterostructures can be effectively controlled by the application of an external electric field, offering a route to an artificial electrostatic modulation of conducing carriers required for realizing oxide electronics and other energy related interfacial materials and devices.

Session CI-4
Coexistence of Superconductivity and Magnetism

CI-4:IL01 **Antiferromagnetism and High-Tc Superconductivity in Cuprates**

H. Mukuda, Graduate School of Engineering Science, Osaka University, Osaka, Japan

Theoretically a relationship between antiferromagnetism (AFM) and superconductivity (SC) is believed to be a key to understand the origin of their remarkably high SC transition in cuprates. Experimentally, however, in a prototype high-Tc copper oxide La2-xSrxCuO4, the AFM and SC phases are separated by the spin-glass phase in association with the carrier localization. In this report, we revealed the intrinsic phase diagram of a homogeneously-doped CuO2 plane based on the site-selective Cu-NMR studies on five-layered cuprates (HM et al., JPSJ 77 (2008) 124706): (1) The AFM metallic state(AFMM) is robust up to Nh ˜ 0.17, (2) the uniform mixing of AFMM and SC takes place at least in 0.14 < Nh = 0.17, (3) Tc has a peak just outside the QCP at which the AFM order collapses, suggesting the intimate relationship between the high-Tc SC and AFM order, namely, the AFM superexchange interaction plays a vital role not only for the onset of the AFM order but also of SC. Although the phase diagram of LSCO are widely believed thus far as typical ones, we claim that the underlying issues in underdoped LSCO may be affected by the disorder and/or by strong 2D fluctuations due to the weak interlayer coupling.

CI-4:IL02 **Coexistence of Superconductivity and Magnetism in Ruthenocuprates**

M. Cuoco, P. Gentile, M. Gombos, A. Vecchione, C. Noce*. Laboratorio Regionale SuperMat, INFM-CNR, Baronissi (SA), Italy and Dipartimento di Fisica “E R Caianiello”, Universita’ di Salerno, Fisciano (SA), Italy

The layered rutheno-cuprate materials RuSr2LnCu2O8 (Ru-1212)and RuSr2(Ln1+xCe1-x)Cu2O10 (Ru-1222) with Ln=lanthanide or Y for both structures, consist of pairs of CuO2 planes alternating with perovskite-like sheets of vertex sharing RuO6 octahedra. Samples of Ru-1212 and Ru-1222 materials were known to show both superconducting and magnetic transitions. Here we review structural and physical properties of these layered compounds mainly focusing on ferromagnetic and superconducting properties and their coexistence/interplay. In particular, we discuss the problem of the coexistence, considering a model which includes two types of carrier responsible separately for these ordered phases. By considering the interplay between a hybridization mechanism and the direct exchange coupling between the two types of carrier, we look at the stability of the coexisting phase assuming also an inhomogeneous superconducting order parameter.

CI-4:IL03 **Inhomogeneous Superconductivity and 1/8 Problem in the Cuprates**

Y. Koike*, T. Adachi, Y. Tanabe, Department of Applied Physics, Tohoku University, Sendai, Japan

First, the possible inhomogeneity of superconductivity has been investigated by means of bulk-sensitive probes, that is, magnetic susceptibility and specific heat in the hole-doped high-Tc cuprate La2-xSrxCuO4, (Bi,Pb)2Sr2CuO6+δ, (Y,Ca)Ba2Cu3O7-δ and in the electron-doped Pr1-xLaCexCuO4+δ. It has been concluded that a phase separation into superconducting and normal-state regions takes place generically in the high-Tc cuprates. Secondly, the electronic ground state of the high-Tc cuprates where the superconductivity is killed by the partial substitution of Ni for Cu has been investigated in La2-xSrxCu1-yNiyO4 from the specific heat and muon spin relaxation. It has been found that the ground state changes from a magnetically ordered state with the strong hole-trapping by Ni to a metallic state with the Kondo effect of Ni with increasing hole-concentration. Thirdly, the Hall coefficient, RH, in the charge-spin stripe-ordered La2-xBaxCuO4 around x = 1/8 has been investigated. It has turned out that RH is zero in the ground state of the charge-spin stripe order at x = 1/8, while RH is negative in the less-stabilized state of the charge stripe for x < 1/8. These are interpreted as being due to the hole-like Fermi surface and the electron pocket originating from the stripe order.

CI-4:L04 **Investigations for the Growth of Large Underdoped Bi2Sr2CaCu2O8+d Single Crystals and Neutron Scattering Measurements**

Sonia De Almeida-Didry*, Fabien Giovannelli, Isabelle Monot-Laffez, LEMA, UMR 6157 CNRS-CEA, Université François Rabelais, Blois, France; Yvan Sidis, Philippe Bourges, Laboratoire Léon Brillouin (LLB), CEA-CNRS, CEA-Saclay, France

In optimally and underdoped regimes, high-Tc copper oxide superconductors exhibit a pseudo-gap state with anomalous properties below a temperature T*, large compared to the superconducting transition temperature, Tc. The origin of pseudogap is a challenging issue as it might eventually lead to identify the superconducting mechanism. To explore the pseudo-gap, we have studied Bi2Sr2CaCu2O8+d (Bi-2212) system in the underdoped regime of the phase diagram. Among high temperature superconducting copper oxide materials, Bi-2212 system has attracted a lot of interest since this system can be easily cleaved and provides high quality surfaces. It has been therefore widely used for the study of electronic excitations using surface sensitive techniques such as ARPES, STM, optical conductivity and electronic Raman spectroscopy. At variance, its magnetic properties have been hardly studied by inelastic neutron scattering technique, since it is still rather difficult to grow large underdoped single crystals. In order to overcome this difficulty, we studied the crystal growth of Bi-2212 by travelling solvent floating zone method (TSFZ). Then different routes have been investigated to obtain underdoped single crystals with volumes larger than hundreds of mm3: influence of low oxygen pressure during the growth, synthesis of Y-doped Bi-2212 and effect of low oxygen pressure annealing on Bi-2212 single crystals. Using polarized elastic neutron diffraction on 4F1 at LLB (CE Saclay), we could identified a hidden magnetic order in the underdoped Bi-2212 system already observed in YBa2Cu3O6+d and HgBa2CuO4+d compounds. We have also carried out a polarized neutron scattering study on IN20 at ILL. The energy scan performed at the antiferromagnetic wave vector (0.5,0.5,14) indicates an excitation located at 40 meV which corresponds to the so-called magnetic resonance peak as observed at Er~5.4kBTc in the superconducting state of optimally doped and overdoped Bi-2212.

CI-4:L05 **Synthesis of Magnetic Nanoparticles and its Application to Obtain YBCO Nanocomposite Thin Films: Ex Situ Approach**

F. Martinez-Julian*, S. Ricart, A. Pomar, A. Palau, J. Arbiol, F. Sandiumenge, T. Puig, X. Obradors; L. Pérez-Mirabet, R. Yáñez, J. Ros, ICMAB-CSIC, Barcelona, Spain

At nanometric scale is possible develop new functional ceramist material where there is high contact surface between two dissimilar materials. New physical and chemical properties are being discovered in these materials. By Chemical Solution Deposition (CSD) two different approaches are used in order to synthesize these FCM. The most general one consist of growing a secondary phase at the same time than the matrix is growing. In this case, tuning the size and shape of the nanoparticles inside the matrix is a very complicated task. We have been exploring a second approach in which previously synthesized nanoparticles are added to the starting precursor solution. This ex-situ approach allows us to control the size and distribution of the secondary phase inside the matrix. In this work we present the synthesis of.magnetic oxide nanoparticles as colloidal suspensions in organic and alcoholic solvents with concentrations in the range of 10-2-10-6M and its using to obtain YBa2Cu3O7 thin films. By following this methodology we expect to improve the superconducting performances in YBCO. The microstructure of the nanocomposite YBCO films was characterized by X-ray diffraction, SEM and TEM. Superconducting properties were measured by both inductive (SQUID) and transport techniques.

Session CI-5

Novel Synthesis and Processing Techniques

CI-5:IL01 Flux-mediated Epitaxy of Complex Oxides

Y. Matsumoto, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan

In the conventional vapor phase deposition the non-equilibrium nature of the process sometimes leads to undesirable crystal quality of the resultant films for complex oxides. The poly-crystallization and the inclusion of impurity phases as well as the serious deviation from the stoichiometry in the film are major problems. In order to overcome these problems, a new concept of “Flux-mediated epitaxy,” (FME) has been proposed as one of the most advanced processes for precise growth control of the complex oxide films and nano-structures. As FME may be a kind of an advanced VLS technique, but its growth control mechanism is completely different from that rationalized in the conventional VLS growth, i.e. more close to the thermodynamic equilibrium process, rather than the kinetic one. In my talk, I will concentrate on the successful application of the FME to nano-engineering of high-Tc superconducting and ferroelectric complex oxide films, and if time permits, would discuss its further potential applications to other materials system.

This work was partially supported by Industrial Technology Research Grant Program in 2007 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

CI-5:IL03 Iron-based Superconductors FeSe and FeTe

Yoshihiko Takano, National Institute for Materials Science, Tsukuba, Japan

Discovery of Fe-based superconductor was received with considerable surprise, since the Fe based-superconductor is expected to be a new series of high-Tc superconductors such as cuprate High-Tc. The FeSe with Tc~13K has the simplest crystal structure among the iron-based superconductors. The structural phase transition from tetragonal to orthorhombic takes place around 70K without magnetic ordering. Surprisingly, the superconducting transition temperature raised from 13K to 37K under the pressure of around 4GPa, which is the third record of Tc in binary compound. On the other hand, analogous compound FeTe shows structural and magnetic transition around 70K, and superconductivity was not observed. Recently we have succeeded to realize superconductivity in FeTe by S doping. We think that the detailed investigation of FeSe and FeTe system will provide us the clues to understand the mechanism of superconductivity in iron-based superconductors.

Y. Mizuguchi et al, Appl. Phys. Lett. 93, 152505 (2008); Y. Mizuguchi et al, Appl. Phys. Lett. 94, 012503 (2009)

CI-5:IL04 Dps Protein as a Bio-reactor to Synthesise Magnetic Nanoparticles

C. Sangregorio*, L. Castelli, L. Sorace, C. Innocenti, D. Gatteschi, INSTM and Dept. of Chemistry, Univ. di Firenze, Sesto Fiorentino, Italy; P. Ceci, E. Chiancone, C.N.R. Inst. of Molecular Biology and Pathology, Dept. of Biochemical Sciences, “Sapienza” Univ. of Rome, Rome, Italy

Up to now, the theoretical approaches to describe the magnetic properties of Molecular NanoMagnets, MNM, and magnetic nanoparticles, MNPs, have been different (quantum mechanic for MNM, while MNPs are treated in a classical way), although the systems themselves are becoming very similar. Indeed, they are both approaching the size of 102 magnetic-centres, MNPs from the top and MNM from the bottom. It is expected that the study of this mesoscopic region will lead to a common view point to describe the two systems, merging the two different approaches. In this contribution a magnetic study on very small iron oxide MNPs through dc, ac and EMR measurements will be presented. MNPs are grown in the cavity of the Dps (DNA-binding protein from starved cells) protein from the bacterium Listeria Innocua. This protein has been chosen because its dimension allows the formation of very small MNPs approaching the typical molecular size. In particular, experimental evidence for the existence of small size effects, like the quantum effects that are typical of MNM will be presented. These results help to develop a common approach for the two classes of systems as well as can provide important information on the role the ferroxidase centres in the iron uptake and storage mechanism.

CI-5:IL05 Bulk Synthesis and Crystal Growth of Magnetic and Superconducting Functional Materials

Toshimitsu Ito, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

I would like to present bulk synthesis and crystal growth of magnetic and superconducting functional materials including a Haldane gap compound Y2BaNiO5 and iron-based superconductors in detail. By the use of high-quality samples, we have revealed fascinating physical properties of the materials. For example, we have discovered magnetic-filed-induced phase transition, using single crystals of Mg-doped Haldane gap system Y2BaNi1-yMgyO5 grown by the traveling solvent floating zone method. We discuss that the edge spins, created by a chain cutting with non-magnetic Mg dopants, are responsible for the field-induced phase transition. For the iron-based superconductors, I will present recent progress in AIST. I would also like to introduce a new type of crystal growth furnace that we have developed recently using lasers instead of halogen lamps as a light (heat) source. I will show the heating method of the furnace and some examples of materials that could be applicable by use of the furnace.

Session CI-6

Oxides with Diluted Magnetic Moments

CI-6:IL01 Magnetism of Dilute Oxides

J.M.D. Coey, School of Physics and CRANN, Trinity College, Dublin, Ireland

Reports of Curie temperatures well above room temperature for thin films and nanoparticles wide-bandgap oxides doped with a few percent of transition-metal cations have triggered intense interest in these materials as potential magnetic semiconductors. The origin of the magnetism is debated; in some systems, the ferromagnetism can be attributed to nanoinclusions of a magnetic secondary phase, but in others, properties are found which are incompatible with any secondary phase, and an intrinsic origin related to structural defects is implicated. The interactions in these materials are qualitatively different from those in magnetically-concentrated compounds, and the standard “*m*-J paradigm” of localised magnetism cannot explain their behaviour. Here we review data on a selection of the most widely-studied materials, highlighting the unusual magnetization curves, which establish that only 1-3% of the volume of the thin films is magnetically ordered. A new model of charge-transfer feromagnetism will be presented, which is able to account for the ferromagnetism of a wide range of defective systems, without the transition-metal dopant participating in the magnetic order.

CI-6:IL02 Electric Field Control of Room Temperature Ferromagnetism in Co-doped TiO2

T. Fukumura, Tohoku University, Sendai, Japan

Ferromagnetic semiconductor is one of the important materials for semiconductor spintronics. Recently, various high Tc ferromagnetic semiconductors, particularly oxides, have been reported. Among them, Co-doped TiO2 reproducibly shows systematic variation of anomalous Hall effect and magneto-optical effect with carrier density[1-4]. Central concern for such high Tc ferromagnetic semiconductors is capability of controlling the ferromagnetism at room temperature. For III-V ferromagnetic semiconductor, electric field control of ferro-magnetism has been already demonstrated at low temperature[5]. Here, we show electric field gating of room temperature ferromagnetism in cobalt-doped TiO2. This result evidences carrier mediated nature of the high Tc ferromagnetism, and leads to room temperature semiconductor spintronics.

[1]H. Toyosaki et al, Nature Mater. 3, 221 (2004); [2]K. Ueno et al, Appl. Phys. Lett. 90, 072103 (2007); [3]T. Fukumura et al, Jpn. J. Appl. Phys. 46, L642 (2007); [4]T. Fukumura et al, New J. Phys. 10, 055018 (2008); [5]H. Ohno et al, Nature 408, 944 (2000)

CI-6:IL03 **Spin Manipulation in Co-doped ZnO**

Heidemarie Schmidt, Forschungszentrum Dresden-Rossendorf e.V., Dresden, Germany

N-type conducting, Co-doped ZnO films prepared by pulsed laser deposition on sapphire substrates have been studied experimentally and theoretically. A large positive MR of 124% has been observed in the film with a low electron concentration, while only a negative MR of -1.9% was observed in the film with a large electron concentration at 5 K. The positive MR is attributed to the quantum correction on the conductivity due to the s-d exchange interaction induced spin splitting of the conduction band. The negative MR is attributed to the magnetic field suppressed weak localization[1]. Voltage control of the electron concentration in Schottky diodes revealed a drastic change of the magnetoresistance and demonstrated the electrically controllable magnetotransport behavior in Co-doped ZnO. The magnetically controllable spin polarization in Co-doped ZnO has been demonstrated at 5 K in magnetic tunnel junctions with Co-doped ZnO as a bottom electrode and Co as a top electrode[2]. There spin-polarized electrons were injected from Co-doped ZnO to a crystallized Al2O3 layer and tunnelled through an amorphous Al2O3 barrier.

[1]Q. Xu, H. S. et al, Phys. Rev. B 76, 134417 (2007); [2]Q. Xu, H. S. et al, Phys. Rev. Lett. 101, 076601 (2008)

CI-6:L04 **A Structural and Magnetic Study of the Hydrogen Mediated Spin Ordering in ZnCoO**

Se-Young Jeong*, Seunghun Lee, Won-Kyung Kim, Dept. of Cogno-Mechatronics Engineering, Pusan National University, Miryang, Korea; Yong Chan Cho, Su Jae Kim, Team of Nano Fusion Technology, Pusan National University; Sungkyun Park, Dept. of Physics, Pusan National University; Il Kyoung Jeong, Chul Hong Park, Dept. of Physics Education, Pusan National University, Korea

The manipulation of spins and magnetism has been one of the most important fields in modern condensed matter physics. The transition metal (TM) doped ZnO is the most promising material with room temperature ferromagnetism for spintronic applications. Here, we report the reproducible manipulation of reversible spin-orderings and its promising potentials for spintronic applications in Co-doped ZnO through the various controls of the injected hydrogen. In both magnetic-circular dichroism and superconducting quantum interference device measurements, the clear ferromagnetism was reversibly produced by the hydrogen-mediated intrinsic spin ordering. This peculiar magnetic reversibility is attributed to the characteristic contribution of hydrogen to interactions with the d-orbitals of TM in ZnO lattice. The results of x-ray photoelectron spectroscopy and the electronic structure using the first-principles calculations consistently support the ferromagnetism associated with the hydrogen position and the contribution of TM ions. The spintronic characteristics of the periodic magnetic domain structure fabricated through selective hydrogenation processes by nano-scaled templates will suggest the new paradigm for manipulating spin ordering of advanced functional materials in molecular-level.

Session CI-7
Spectroscopy of Magnetic Oxides

CI-7:IL01 **Modeling Highly Resolved Spectroscopies of Complex Materials: From Qualitative to Quantitative**

Arun Bansil, Physics Department, Northeastern University, Boston, Massachusetts, USA

We stand at the threshold of a new “golden age” of spectroscopic studies of materials for unraveling how charge, spin, orbital and lattice degrees of freedom interact to produce emergent phenomena and exotic states of matter. The need for realistic modeling of various highly resolved spectroscopies is thus becoming of critical importance in providing discriminating tests of competing theoretical models and as a rational basis for future experimentation. I will discuss how as we model spectroscopic data from a qualitative to a quantitative level, surprising new insights into the nature of electronic states and correlation effects are obtained in high-Tc cuprates and other complex materials. Illustrative examples in cuprates include: (i) Asymmetry of the scanning tunneling spectrum between positive and negative bias voltages and the extent to which it comes about within the conventional picture; (ii) Origin of the “high-energy kink” or the “waterfall effect” in the photoemission spectrum as an interplay between matrix element and self-energy effects; and (iii) The nature of the dichroic signal in photoemission and its relationship to the time-reversal symmetry breaking in the cuprates. I will also comment on our recent work on the manganites and topological insulators.

CI-7:IL02 **New Electronic States in the Magnetic Materials Revealed by ARPES**

Changyoung Kim, Dept. of Physics, Yonsei University, Seoul, Korea

Over the last 2 decades, we have seen a dramatic improvement in the ARPES technology. As a result, ARPES has played a crucial role in resolving many issues in solid state physics as well as in finding new electronic states in many materials. In this presentation, I will talk about basic principles and current status of ARPES technology as well as information one can obtain from ARPES spectral functions. What is the physical principle behind ARPES? What are challenges in realizing ARPES? How were they solved? Then, I will talk about how ARPES is used in the studies on electron systems with many-body interactions and what it has accomplished. Two examples on new electronic states observed by ARPES will be presented. The first one is the J=1/2 Mott insulating states found in Sr2IrO4. I will discuss how Coulomb repulsion in combination with spin-orbit coupling can bring about new Mott insulating states J=1/2 instead of the ordinary S=1/2. The other example is on the recently found topological insulators. These insulators are supposed to have special surface metallic states that are topologically protected. Properties of the topological states will be discussed in terms of Rashba effect as well as quantum Hall effect, along with experimental evidences for the states.

CI-7:L03 **RE L_3 X-ray Absorption Study of $REO_{(1-x)}F_xFeAs$ (RE = La, Pr, Nd, Sm) Oxypnictides**

B. Joseph[1], A. Iadecola[1], M. Fratini[2], A. Bianconi[1], A. Marcelli[3], N.L. Saini[1]*, [1]Dipartimento di Fisica, University of Rome "La Sapienza", Roma, Italy; [2]Istituto di Fotonica e Nanotecnologie, CNR Roma, Italy; [3]Laboratori Nazionali di Frascati, INFN, Frascati, Italy

Rare earth L_3-edge x-ray absorption near-edge structure (XANES) spectroscopy has been used to study REOFeAs (RE = La, Pr, Nd, Sm) oxypnictides. The Nd L_3 XANES due to the 2p_(3/2) to 5d transition shows a substantial change in both white line spectral weight and the higher energy multiple scattering resonances with the partial substitution of O by F. A systematic change in the XANES features is seen due to varying lattice parameters with ionic radius of the rare earth. On the other hand, we hardly see any change across the structural phase transition. The results provide timely information on the local atomic correlations showing the importance of the local structural chemistry of the REO spacer layer and interlayer coupling[1, 2] in the competing superconductivity and itinerant striped magnetic phase of the oxypnictides.

[1]B. Joseph et al, J. Phys.: Condens. Matter, 21, 432201 (2009); [2]A. Iadecola et al, EPL, 87, 26005 (2009)

CI-7:IL04 **Photoemission Spectroscopy of Perovskite-type Oxides under Epitaxial Strain**

A. Fujimori, Department of Physics, University of Tokyo, Tokyo, Japan

The physical properties of strongly correlated electron systems are generally sensitive to pressure, but unfortunately it is impossible to carry out photoemission experiment under hydrostatic pressure. Instead, it is possible to perform photoemission experiment under uniaxial pressure using thin films which are epitaxially grown on single-crystal substrates. In this talk, the following results will be presented: i) Distortion of Fermi surfaces in SrVO3 grown on SrTiO3 (STO). ii) Suppression of incommensurate fluctuations in Pr1-xCaxMnO3 grown on LaAlO3 (LAO)[1]. iii) Metal-insulator transition[2] and Madelung potential shifts[3] in La1-xSrxMnO3 grown on STO, LSAT, and LAO.

This work has been done in collaboration with H. Wadati, S. Aizaki, S. Ideta, T. Yoshida, K. Yoshimatsu, M. Minohara, A. Maniwa, A. Chikamatsu, K. Horiba, I. Ohkubo, H. Kumigashira, M. Oshima, S. Ueda, H. Yoshikawa, E. Ikenaga, J.J. Kim, K. Kobayashi, M. Lippmaa, M. Kawasaki, H. Koinuma, T. Mizokawa, and G.A. Sawatzky.

[1]H. Wadati et al, Phys. Rev. Lett. 100, 026402 (2008); [2]K. Horiba et al, Phys. Rev. B, in press; [3]H. Wadati et al, Phys. Rev. B 80, 125107 (2009).

CI-7:IL05 Manipulation Electronic Structure by Laser Pump-photoemission Probe in Oxides

T. Mizokawa, Department of Complexity Science and Engineering, University of Tokyo, Tokyo, Japan

Transition-metal oxides show surprisingly rich electric and magnetic properties due to the strongly correlated d electrons with spin, charge, and orbital degrees of freedom. In particular, frustrated electronic states under multi-phase competition can be realized in some transition-metal oxides with strong electron-lattice coupling and show drastic responses to external stimuli such as optical excitation. Here, we report on photoemission studies of Pr0.55(Ca1-ySry)0.45MnO3 (PCSMO, y=0.25,0.40), Ti1-xCoxO2 (x=0.05, 0.10), and SrTiO3 under laser illumination and discuss unusual electronic structure changes induced by optical excitation in these strongly correlated oxides. The drastic photo-induced electronic structure change in the Mn oxides with eg electrons can be understood on the basis of Jahn-Teller distortion and is in interesting contrast to the Ti oxides with t2g electrons.

The present work has been done in collaboration with Y. Fujiwara, N. Takaiwa, N. Yamashita, K. Takubo, J.-Y. Son, J. W. Quilty, N. Takubo, K. Miyano, Y. Yamada, H. Toyosaki, T. Fukumura, M. Kawasaki, M. Takesada, T. Ishikawa, S. Koshihara, M. Itoh and E. Hanamura.

Session CI-8

Quantum Phase Transitions and Magnetism in Oxides

CI-8:IL01 Quantum Critically in Low Dimensional Oxides

Thierry Giamarchi, University of Geneva, Geneva, Switzerland

Although we now know that strongly correlated systems can have several type of conventional order ranging from magnetism to superconductivity, the possibility that they present also more exotic phases remains an elusive but very challenging question. In particular whether such systems can have orbital current order has been strongly debated, in the context of the pseudogap phase of High Tc oxydes. This question can be looked at in a controlled way on the one dimensional (ladder) version of this problem. I will present the results we obtained and discuss in particular the comparison between the case of a simple Hubbard ladder[1] versus a three band model (Cu-O ladder)[2]. For the two-dimensional case, we have performed a variational Monte Carlo analysis for a three band Cu-O model[3]. I will discuss the phases obtained by this approach as well as the possible experimental consequences.

These works are a collaboration with E. Orignac; P. Chudzinski and M. Gabay; C. Weber, A. Lauchli and F. Mila.

[1]E. Orignac and T. Giamarchi, PRB 56 7167 (1997); [2]P. Chudzinskii, M. Gabay and T. Giamarchi, PRB 76, 161101 (R) (2007); PRB 78, 075124 (2008); [3]C. Weber, A. Lauchli, F. Mila and T. Giamarchi, PRL 102, 017005 (2009).

CI-8:IL02 Intrinsic Lattice Instabilities in Magnetic Oxides Close to the Metal-insulator

F. Rivadulla, Physical Chemistry Department, University of Santiago de Compostela, Santiago do Compostela, Spain

On approaching the itinerant-electron regime from the localized side in an oxide, the ionic image of the solid implicit in the crystal field and superexchange theories must break down at some point. Then, there must be a fundamental change in the nature of the chemical bond associated to the metal-insulator transition. Whether this change occurs discontinuously or implies the coexistence of localized/itinerant electrons (or even a new thermodynamic phase) is not clear at the moment, in spite of being a key for the understanding of the complex behavior of doped Mott-insulators. In this talk we will review some of our recent experiments in localized, single-valence transition-metal oxides, in which pressure is used to drive the systems close to the itinerant electron crossover. We have found evidences of the existence of a new phase between the localized and the itinerant-electron state, in which molecular-cation superstructures are formed in the solid. The magnetic, electric and structural properties of this state will be discussed in different systems. We will show that the coupling of the lattice and electronic degrees of freedom is intrinsic to the proximity to the localized-to-itinerant quantum phase transition.

CI-8:IL04 Novel Behaviour Near Quantum Phase Transitions and Beyond

Siddharth S. Saxena, Cavendish Laboratory, University of Cambridge, Cambridge, UK

Low dimensionality is generally considered as a necessary ingredient for high superconducting transition temperatures. Surprisingly, perhaps, systems based on graphite have received little attention in this context. Introducing metal atoms between the carbon layers can tune the interlayer spacing and charging of the graphite host through a variety of electronic ground states. One such ground state is superconductivity, which is not present in pure graphite. Here we report the discovery of superconductivity in the intercalation compounds C6Yb and C6Ca, with transition temperatures of 6.5 and 11.5 K, respectively. These critical temperatures are unprecedented in graphitic systems and have not been explained by a simple phonon mechanism for the superconductivity. This discovery has already stimulated several proposals for the superconducting mechanism that range from coupling by way of the intercalant phonons through to acoustic plasmons. Going beyond metallic and superconducting systems, case for quantum critical behaviour in ferroelectric systems will be discussed.

CI-8:IL05 Universality Classes for Coulomb-frustrated Phase Separation. From Incommensurate Charge Density Wave to Stripes

C. Di Castro, Dipartimento di Fisica, Università "La Sapienza", Roma, Italy

In strogly correlated electronic systems we individuate two universality classes for Coulomb-frustrated phase separation and discuss universal aspects of their phase diagram in 2D and 3D. In the case of negative short-range electronic compressibility, relevant for Cuprates, the transition from homogeneous- to inhomogeneous-states starts at a finite value of frustration in the form of incommensurate charge density wave. For weaker frustration, it continuously evolves into aggregates of sharp structures with different morphologies allowing for a stripe phase in 2D.

C. Ortix, J. Lorenzana and C. Di Castro , J. of Phys. Condens. Matter 20, 434229 (2008); Physica B: Condensed Matter 404, 499 (2009); Phys. Rev. Lett. 100, 246402 (2008) and in preparation.

CI-8:IL06 Quantum Critical Fluctuations in the Frustrated Kondo Lattice $Pr_2Ir_2O_7$

M. Brando*, J.G. Donath, F. Steglich, Max Planck Institute for Chemical Physics of Solids, ,Dresden, Germany; P. Gegenwart, I Institute of Physics, University of Gottingen, Gottingen, Germany; S. Nakatsuji, Institute for Solid State Physics, University of Tokyo, Tokyo, Japan

The Kondo lattice oxide $Pr_2Ir_2O_7$ is located near a quantum phase transition between an antiferromagnetic ordered phase and a paramagnetic one, where magnetic quantum fluctuations are supposed to become critical. Instead of finding signatures of a quantum critical point, magnetic and thermodynamic experiments have suggested a peculiar metallic spin-liquid ground state. In fact, due to the arrangement of the Pr *f*-moments in the highly geometrically frustrated pyrochlore lattice, frustration is so strong that prevents magnetic long-range order - despite an antiferromagnetic RKKY interaction of about 20 K - and favors such a novel state below $T_{SL} \sim 1.7$ K. We have investigated the temperature dependence of the quantum critical fluctuations in the spin-liquid state by means of thermal expansion $\alpha(T)$ and specific heat C(T) measurements on a single crystal down to T = 0.05 K. The quantity $\Gamma(T) = \alpha(T)/C(T)$ is known as Gruneisen ratio and its divergence provides direct evidence for the presence of such fluctuations. Indeed, we have found a divergent behavior: $\Gamma(T) \sim T^{-0.55}$.

Poster Presentations

CI:P02 Comprehensive Study of Mn doped-ZnO Thin Films Grown by rf Sputtering and Ion Implantation Techniques

A.G. Rolo, M.F. Cerqueira, F. Oliveira, T. Viseu*, J. Ayres de Campos, T. de Lacerda-Arôso, M.I. Vasilevskiy, Centro de Física, Universidade do Minho, Braga, Portugal; J.S. Martins, N.A. Sobolev, I3N and Dpto de Física, Universidade de Aveiro, Aveiro, Portugal; E. Alves, ITN, Ion Beam Laboratory, Sacavém, Portugal

ZnO:Mn transparent thin films with the Mn contents ranging from 1.8 to 3.25 atomic % were investigated. The layers were grown by RF magnetron sputtering and the doping with Al, and Mn was achieved either by co-sputtering or by ion implantation with subsequent annealing. The samples were characterized by means of XRD, RBS, Hall Effect measurements, and optical absorption spectroscopy. The films are nanocrystalline, with wurtzite-structure grains of a typical size of 20 nm. A comparative Raman spectroscopy study of (Mn, Al)-doped and undoped ZnO layers is presented. First-order Raman response measured under ë=514.5 nm, 488 nm, and 325 nm excitation are discussed. It is shown that doping with any of the impurities used in this work produces a strong enhancement of the LO phonon band, which is attributed to the (dipole-forbidden) intra-band Frohlich mechanism. According to the Raman spectroscopy data, Mn mostly substitutes Zn in the lattice sites. In spite of these factors, namely, the nanostructure of the layers and the Mn(Zn) substitution, that are considered favorable for ferromagnetism in this material, both magnetic resonance and Faraday effect measurements show paramagnetic behaviour of the ZnO:Mn films and absence of ferromagnetic order at room temperature.

CI:P04 **Phase Coexistence in Nano-sized (La,Ca)MnO3 Manganites Investigated by Neutron Powder Diffraction and Magnetization Measurements**

M. Ferretti*, A. Martinelli, CNR-INFM-LAMIA, Genova, Italy; M.R. Cimberle, CNR-IMEM, Genova, Italy

Several evidences of nanophase inhomogeneities at low T have been observed that insert the study of manganites in the context of natural or self-assembled nanostructured materials. Studying the natural nanophase separation of manganites on compounds having also nanometric grain size it should be possible to evidence an influence on the magnetic properties of such materials. Magnetic measurements evidenced the arising of FM on cooling in nanometric samples of (La0.50Ca0.50)MnO3 and (La0.25Ca0.75)MnO3 whereas in micrometric sized samples of these compounds the AFM component notoriously prevails over the FM one at low temperature. On the contrary the ferromagnetic transition broadens and decreases as grain dimensions reduce down to the smaller grain size sample for which FM is strongly suppressed in (La0.63Ca0.37)MnO3. Samples characterized by a different average nanometric particle size for each composition have been prepared by sol-gel synthesis. All samples have been characterized by XRD and HRTEM. Magnetic properties have been investigated by means of dc and ac magnetic measurements in the temperature range 5-350 K. NPD analysis has been also carried out to test the coexistence between FM and AFM component in nano-sized powders.

CI:P05 **Multiferroic Mn-doped BaTiO3 Thin Films**

Yao Shuai*, Danilo Buerger, Lin Li, Shengqiang Zhou, Manfred Helm, Heidemarie Schmidt, Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, Dresden

Strain imposed by coherent epitaxy of BaTiO3 (BTO) thin films grown by reactive molecular beam epitaxy and by pulsed-laser deposition (PLD) on GdScO3 and SrRuO3 substrates can result in a ferroelectric transition temperature of nearly 500°C higher and a remanent polarization at least 250% higher than BTO single crystals[1]. We used PLD to grow Mn-doped BTO thin films on ZnO, MgO, and c-plane Al2O3 substrates from ceramic targets with 5at% Mn. The lattice mismatch between Mn-doped BTO and MgO, c-Al2O3, and ZnO amounts to 3.4%, 16.0%, and 22.8% respectively. For example, we observed XRD reflexes of (00l)- and (l00)-oriented a domains on Mn-doped BTO deposited on ZnO which indicates that the Mn-doped BTO films are polycrystalline. At room temperature the saturated magnetic moment of Mn-doped BTO films with a thickness of 500nm on MgO substrates amounts to 1.8 emu/cm3. The observed induction of magnetism in the Mn-doped BTO proves the feasibility to add spin functionality to BTO on different substrates.

[1] K.J. Choi et al, Science 306 (2004) 1005.

CI:P08 **Characterization of Mn-doped ZnO/Al2O3 Multilayered Nanostructures Grown by Pulsed Laser Deposition**

A. Khodorov[1], S. Levichev[1], O. Karzazi[2], A. Chahboun[1, 2], A.G. Rolo[1]*, N.P. Barradas[3], E. Alves[3], C.J. Tavares[1], D. Eyidi[4], J.-P. Rivière[4], M.F. Beaufort[4], M.J.M. Gomes[1], [1]Physics Centre, University of Minho, Campus de Gualtar, Braga, Portugal; [2]LPS, Physics Department, Faculty of Sciences, Fes, Morocco; [3]ITN, Ion Beam Laboratory, Sacavém, Portugal; [4]PhyMat, University of Poitiers, Futuroscope-Chasseneuil, France

In recent years, ferromagnetism in semiconductors received significant interest due to the potential applications in spintronics. Doped ZnO was predicted to show ferromagnetism at room temperature. In this work, ZnMnO nanocrystals embedded in Al2O3 were grown by pulsed laser ablation technique for spin memory applications. The crystalline structure and morphology of the nanostructures were characterized by Raman spectroscopy, grazing incidence X-ray diffraction (GID), grazing incidence small angle X-ray scattering (GISAXS), and high resolution transmission electron microscopy (HRTEM). The chemical composition was studied using RBS and PIXE measurements. The results are analyzed and discussed.

CI:P09 **Electron Spin Resonance of Nickelate Lanthanum**

N. Poirot*, LEMA, UMR 6157 CNRS - CEA, Université François Rabelais, Tours, France; R.A. Souza, Swiss Light Source, Paul Scherrer Institut, Villigen PSI, Switzerland

In the present study we focused on the nickelates system, which present more stable stripe order and allow a large domain of doping. More specifically, we studied the non-stoichiometric system La2NiO4+x (LNO), in which the extra oxygen tend to order, and that has been less studied than the chemically doped system, where the dopants are randomly distributed. (ESR) technique has been chosen due to its sensibility to microscopic magnetic fluctuations. Moreover, this technique has already proved to be sensitive not only to magnetic, but also to charge ordering We present a systematic study of the charge and spin fluctuations in oxygen doped nickelates to get insight into the dynamic of the system using ESR. The intrinsic resonance signal of polycrystalline La2NiO4+x with x-values 0.09, 0.12 and 0.17 have been studied, in a large temperature range (10K < T < 300K). The x = 0.12 compound has been chosen as a starting point, since neutron diffraction studies in composition very close to this value14 have well characterized the stripe order in this system, showing that the holes order at around TCO = 200K, while the spins order at TS = 110K. By analogy, the ESR results on this compound allowed us to interpret the results in the other two compounds.

Symposium CJ

SCIENCE AND TECHNOLOGY FOR SILICATE CERAMICS

Oral Presentations

Session CJ-1
Science of Silicate Ceramics

CJ-1:IL01 **New Silicate Glass-ceramic Materials and Composites**

D. Hotza*, A.P. Novaes de Oliveira, Group of Ceramic and Glass Materials (CERMAT), Department of Mechanical Engineering (EMC), Federal University of Santa Catarina (UFSC), Florianópolis, SC, Brazil,

New silicate glass-ceramic systems have been investigated due to their interesting chemical, mechanical and thermal properties. Glass-ceramics based on β-spodumene and zircon crystalline phases have shown good chemical resistance, high bending strength as well as high abrasion resistance, when compared with traditional ceramic materials, and coefficient of thermal expansion from 4.6 to 9.1x10-6 °C-1. These features basically depend on the nature, size and distribution of the formed crystals as well as on the residual glassy phase. The nature of the formed crystalline phases and consequently the final properties can be controlled by modifying the chemical composition of the parent glass and also by adequate selection of the heat-treatment parameters. The classical fabrication of glass-ceramic materials consists on the preparation of monolithic glass components followed by heat treatments for crystallization. An alternative is the production of glass-ceramics processed from glass powders and consolidated by sintering using the same equipments of traditional ceramic plants. This work reports the manufacturing and characterization of glass-ceramic materials and composites processed by uniaxial pressing, injection moulding, extrusion, tape casting and rapid prototyping.

CJ-1:IL02 **Characterisation of Microstructure and Crystallographic Texture of Ceramics**

Daniel Chateigner, CRISMAT-ENSICAEN, IUT-Caen, Université de Caen Basse-Normandie, Caen, France

The elaboration of advanced ceramics points more and more to the necessity of complex characterisations, in the aim of determining phase fractions, structures, microstructures, textures, porosities. This has for long limited the use of full x-ray diffraction analysis, because such ceramics often exhibit complex diffraction patterns with a lot of peak overlaps. Such a behaviour is even more pronounced when peak shapes are strongly asymmetric like in the case of silicate turbostratic stacks. The Combined Analysis formalism was developed recently which offers a large capacity in resolving the former problem, when using ray diffraction analysis tools. Furthermore, such an approach prevents from biases introduced in the determination of, for instance, microstructure parameters, when they are coupled with other parameters, like texture for instance. We will illustrate the Combined Analysis approach on examples of characterisations of single and multiphase ceramics exhibiting textures, crystallite sizes and microstrains, and turbostratic behaviours. We will see that not only the texture, but the structure, the residual stresses, phase contents and microstructures become available at once when using such a technique, which only requires some instrumental ressources at a lab level.

CJ-1:IL03 **Effect of Compositional Modification on Sintering Behaviour and Microstructures of Porcelain Tiles**

F. Kara*, A. Kara, Anadolu University, Department of Materials Science and Engineering, Eskisehir, Turkey; P. Dag, Seramik Arastirma Merkezi, Teknoloji Gelistirme Bolgesi, Eskisehir, Turkey; M. Tuna, Kutahya Seramik, Kutahya, Turkey; H. Kiran, Ege Seramik, Izmir, Turkey

Production of glazed and unglazed porcelain tiles are increasing due to their better properties and market values. Firing of porcelain tiles requires longer cycle times and/or higher temperatures. In addition, lighter body colour requirement necessitates the use of purer clays. These requirements make porcelain tile production more costly. Therefore, there is an interest in development of porcelain tile compositions that will fire faster and/or at lower temperatures in order to lower the cost of firing and that will also enable lower quality raw materials to be used without substantially degrading the fired colour. In this presentation, body composition of a porcelain tile was systematically varied in order to see its effect on firing behaviour and phase development. It is possible to reduce firing time and temperature of porcelain tile substantially by proper adjustment of alkali/alkaline earth ratio. It was also revealed that by forming crystalline phases in the microstructure that are able to incorporate iron into their crystal structure, less quality clays can be used without degrading the body colour substantially. Furthermore, adjustments of alkali/alkaline earth ratio can be extended to sanitaryware bodies to realise substantial reductions in firing temperature.

CJ-1:IL04 **Glass Ceramic Systems Suitable for Conventional Ceramic Glazes**

Bekir Karasu, Anadolu University, Department of Materials Science and Engineering, Eskisehir, Turkey

In the recent years glass-ceramic systems became industrially important for their high softening point, good coating capability for relevant substrates, high chemical and abrasion resistance. Glass-ceramic materials belonging to the ZrO2-CaO-MgO-SiO2 (ZrCMS) and CaO-MgO-Al2O3-SiO2 (CMAS) systems were studied for porcelain tile glazes and found to be rather hard and to indicate high resistance to wear and scratches. The ZrCMS glass-ceramic system exhibits high resistance to abrasion and surface scratches thanks to the diopside crystals forming during firing. The CMAS system is of importance in terms of high hardness and abrasion resistance with its glass ceramic side with a major phase of anorthite. Zircon containing frit based opaque glazes are widely used in ceramic wall tile industry. However, high zircon cost, continuous and rapid consumption of zircon sources lead to develop new frits and glazes with zircon content on a limited scale or even with no zircon. In such a term the K2O-MgO-CaO-BaO-ZrO2-B2O3-Al2O3-SiO2 systems were studied to prepare fast single-fired wall tile glazes.

CJ-1:IL05 **New Development in the Non Contact Measurement of Thermo-mechanical Properties of Materials**

Mariano Paganelli*, Expert System Solutions Srl, Modena, Italy; Daniele Paganelli, Facoltà di Ingegneria dei Materiali, Università di Modena, Italy

The optical measurement of thermo-mechanical properties allows the sample to be completely free from constraints. This enables the possibility to measure the true change in size or volume of a material during a sintering process. Thanks to the fact that the measure is carried out with no contact in becomes possible to carry out other measurements during the test, like the change in mass. Joining a double beam optical dilatometer and an electronic scale we can measure simultaneously the change in size with a resolution of one part over 100.000 and the change in weight of the specimen, with a resolution of 1 part over 10.000. Moreover, thanks to a innovative temperature controller design, the heat treatment can be designed with complete freedom, even from a mathematical formula (i.e. sinusoidal or exponential) and it can be controlled by the change in size of the specimen during the test. This makes it possible to perform the controlled rate sintering (shrinkage) even if the driving force of the sintering process is the viscous flow of glassy phases, like in traditional ceramics. Case study: near zero shrinkage sintered bodies for traditional ceramic in fast firing cycle.

CJ-1:L06 **Use of Iron-rich Slag as Raw Material for Production of Glassy and Glass-ceramic Pyroxene Materials**

Erika Iveth Cedillo González[1], Juan Jacobo Ruiz Valdés[1, 2]*, Anabel Álvarez Álvarez Méndez[1], [1]Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Monterrey, N.L., Mexico; [2]Centro de Innovación, Investigación y Desarrollo en Ingeniería y Tecnología CIIDIT, Universidad Autónoma de Nuevo León, Apodaca, N.L., Mexico

Highly siliceous metallurgical wastes are produced at very large amounts around the world, and so they have been become into a global enviromental problem. Actually, alternative ways to use these wastes are proposed to put an end to pollution and, at the same time, to generatesome additional benefits. In this work, glass and glass-ceramic materials were prepared from mixtures of iron-rich metallurgical slags and soda lime recycled glass. The obtained materials were characterized by X-ray fluorescence, X-ray diffraction, differential thermal analysis and scanning electron microscopy. A working range compositional range of 30-70 wt.% of slag in the mixture of recycled glass-slag succesfully generated stable glasses by fusion at 1450 °C/2h. In the range of 45-58 wt.% of slag, glasses without spontaneuos crystallization were obtained. Secondary thermal treatments to the glasses to form glass-ceramics were performed with datafrom differential thermal analysis. The main crystalline phases developed in the glass-ceramics with low content of slag werw within the pyroxene group and a magnetite phase was present in glass-ceramics with high content of iron-rich slag. Glasses ans glass-ceramics thus formed are sucepible to be used as flooring and tiling materials for buildings.

CJ-1:IL08 **Use of Phase Diagrams to Guide Ceramic Production from Alternative Raw Materials**

Ana M. Segadaes, University of Aveiro, Department of Ceramics and Glass Engineering (CICECO), Aveiro, Portugal

The desire for higher and healthier living standards drives industrial activity, which drags with itself two environmental difficulties: it ultimately feeds on natural non-renewable resources and it produces increasing amounts of wastes or sub-products, subjected to stricter disposal legislation. Thus, industry faces two concerns: natural raw materials are getting more scarce and expensive and waste materials are now a burden with a raising price tag on it. Today, industries are using alternative natural raw materials and have optimised their processes, hence producing less waste. Clay-based ceramic products are very heterogeneous and can easily tolerate raw material changes, including the incorporation of waste materials (inertization of hazardous wastes). What has been overlooked too often is the fact that some wastes and sub-products are similar in composition to the traditional natural raw materials and often might even be beneficial in the fabrication process. Thus, upgrading wastes to alternative raw materials becomes technically and economically interesting. This paper shows how to use phase diagrams to make educated choices of compositions and processing parameters, save time and resources and eventually ameliorate the negative impact of wastes on the environment.

CJ-1:IL09 **Clay Structural Transformations During Firing**

P. Blanchart*, S. Deniel, N. Tessier-Doyen, GEMH, ENSCI, Limoges, France

In clay ceramics, mullite is the most important recrystallized phase with a range of morphology and stoichiometry. Variables affecting the mullite formation include the clay mineral type and behavior during heating, and the occurrence of liquid and impurities as Fe. This presentation will review recent research, looking at structural transformations in some typically used phyllosilicate systems: (i) structural transformations of kaolinite and mica were identified at temperature up to 1100°C. They evidence a residual structural order of high temperature phases which is favorable to the topotactic recrystallization of mullite; (ii) from the high temperature form of phyllosilicates, an organized network of mullite can be obtained; (iii) the composition of a local and transient liquid and the presence of minor elements as Fe has a significant influence on the mullite morphology; (iv) mechanical properties are closely related to size and organization degree of the mullite network; (v) the process itself influence the kinetic of structural transformations and particularly the powder compact density and the thermal cycle. These researches in silicate ceramics evidence multiple and complex challenges, providing opportunities for future development.

CJ-1:L10 **Effect of Marl Addition on the Properties of Wall and Floor Tile Bodies**

Kagan Kayaci[1], Alpagut Kara[2, 3]*, Z. Emel Oytaç[1, 3], Can Genç[4], [1]Termal Seramik Sanayi Ltd., Bilecik, Turkey; [2]Anadolu University, Dept. of Material Sci. and Eng., Eskisehir, Turkey; [3]Ceramic Research Center, Eskisehir, Turkey; [4]Istanbul Technical University, Dept. of Geological Eng., Istanbul, Turkey

In this study, the effect of marl incorporation in varying amounts into commercial wall and floor tile formulations were investigated in detail. The marl was supplied from the Gölpazari flysch which is Upper Cretaceous in age, northwestern part of Osmaneli town (Bilecik city, NW Turkey) and used as the raw material. The Gölpazari flysch is composed of sandstone, siltstone, mudstone and marl alternation forming the relatively upper part of the Mesozoic sedimentary succession of the Sakarya zone. Firstly, the chemical and mineralogical properties of the marl were determined. Then, a number of wall and floor tile compositions were prepared containing marl up to 8 wt. %. The vitrification behavior of the standard bodies together with the marl containing bodies was evaluated using a double-beam optical non-contact dilatometer. In addition, XRD was used to analyze the phases which were formed after firing. SEM was also employed in order to observe the microstructural characteristics of the selected fired bodies with respect to increasing marl content. Physical, thermal and optical properties of all the investigated bodies were measured. According to the results, it was possible to use marl into wall and floor tile formulation as an alternative raw material and to obtain meaningful technological properties.

CJ-1:L11 **The Role of the Kaolinite-mullite Reaction Sequence in Moisture Mass Gain in Fired Kaolinite**

H. Mesbah*, M.A. Wilson, M.A. Carter School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, Manchester, UK

Kaolinite (2SiO2.Al2O3.2H2O), an aluminosilicate mineral, is the most common constituent mineral in clay used in manufacturing traditional ceramics such as whitewares, some refractories and structural clay products. On firing, kaolin (mainly kaolinite) undergoes several phase transformations. Immediately following firing, kaolin starts to chemically combine with atmospheric moisture. This reaction causes a mass increase that is proportional to the fourth root of time. The consequence of this mass gain is an accompanying expansive strain. Kaolinite transformations following firing at a range of temperatures between 700 and 1200 °C were examined by XRD. Following firing, high accuracy mass gain measurements were carried out using a microbalance under precisely controlled conditions of temperature and relative humidity. It was found that the formation and development of crystalline phases increases with increasing firing temperature. This causes a reduction in the amorphous phase which, in turn, leads to reduced mass gain. Kaolin fired at 1200 °C exhibited the least reactivity with moisture and mullite was found to be the dominant crystalline phase after firing at that temperature. SEM was used to examine microstructural changes in the fired specimens. The reactivity of the ceramic with moisture is shown to be directly related to the crystallinity of the fired clay.

CJ-1:IL12 **Synthesis and Properties of Hybrid Lamellar Silica**

G. Toussaint, C. Henrist, R. Cloots*, Chemistry of Inorganic Materials, University of Liege, Liege, Belgium

Compared to composites with conventional particles as filler, only a few percents of well-dispersed lamellar nanofillers is sufficient to greatly change composite properties. This significant properties improvement is however strongly dependent on the filler - matrix interactions, so that comprehensive studies of the fillers structure and surface properties have been therefore greatly encouraged for a better understanding and the development of improved nanocomposites. Among the group of lamellar fillers, which includes the well-studied natural clays, synthetic lamellar silicas are very promising materials which could be used as unique model for the study of nanocomposites properties. These fillers can be easily prepared by liquid crystal templating and their surface easily tuned by silanation in order to obtain lamellar organic-inorganic hybrids. Among our laboratory, several studies have been therefore focused on the preparation and characterization of these lamellar particles. An in-depth investigation of these fillers preparation, surface, structure and morphological properties will be discussed in this paper.

CJ-1:IL13 **Simple Rheological Tests and Protocols for SME Ceramic Producers**

C. Galassi, D. Gardini*, CNR-ISTEC, Faenza, Italy

The rheological behaviour of ceramic suspensions affects the quality of the products and the yield of the processes, therefore its control is advisable to obtain materials with enhanced properties and to reduce the energy consumption. The importance of such a control in cast slips, slurries for spray-drying, screen-printing inks, ink-jet printing inks, glazes, either for Quality Control aims or to formulate the systems, is well-known from many years. As in these control procedures the determination of the rheological behaviour is a critical point, this work is focused on the assessment of the viscosity (flow behaviour) and its dependency on time (thixotropy). The ceramic factories are still currently widely using simple and cheap instruments to find these behaviours (or something related to it). However, the information they can supply are, in some cases, limited and not completely satisfying, therefore optimizing the procedures is important to improve reproducibility and precision. Suggestions about simple tests and protocols applicable with the viscometers available in the ceramic factories are given. The protocols include, beyond the test itself, all the steps that can affect the results, as the thermo-mechanical history undergone by the samples before testing.

Session CJ-2
Innovation in the Silicate Ceramics Industry

CJ-2:IL01 **Long-term Optical and Thermal Examinations of Ceramic Wall System with Solar-altitude Dependent Reflectance**
Hiroshi Kakiuchida, Materials Research Institute for Sustainable Development, National Institute of Advanced Industrial Science and Technology, Nagoya, Japan

Many ceramic tiles are used for outer walls of building, and their solar absorption affects heat flow into room and residential comfortability. Particularly in the region where great temperature change is annually experienced, different photothermal properties between summer and winter are desired for the wall surfaces. On the other hand, solar altitude changes throughout the year, and thus ceramic wall with solar-altitude dependent reflectance is regarded to be effective for autonomous control of heat flow into room. In this study, triangular-shaped ceramic walls with high and low solar reflectance on upper and lower surfaces, respectively, were proposed and the effect was examined. Firstly, this concept was evaluated by ray-tracing simulations in consideration of meteorological data, diffusive surface and reflectance spectra of ceramic tiles and glazes. The simulations expected several-percent difference in solar absorption between winter and summer, and they suggested an ideal shape to obtain the large difference, that is, high diffuse reflectance of upper surface of the triangular-shaped tile. Photothermal properties of the tile were experimentally examined in outdoors for months, and the consistency and discrepancy against the estimations were discussed to be analyzed.

CJ-2:L03 **Consolidation of Sand by Alkaline Silicate Solution**
S. Lucas*, J. Soro, S. Rossignol, GEMH-ENSCI, Limoges, France; J-L. Gelet, Ferraz-Shawmut, Saint Bonnet-de-Mure, France

The consolidation of sand by alkaline silicate solution is relevant today for the cement setting comprehension. One field application is in electrical protection where the fuse technology is continuously in progress to reduce cost and to the quality environment. In this context, this work concerns the agglomeration behaviours of sand with alkaline silicate solution. The effect of sand particles size and concentration of solutions are investigated at various temperatures. The main objective is the understanding of the interactions between sand and this alkaline solution. Impregnating in alkaline silicate solution and drying elaborate the various consolidated materials. Investigations included thermogravimetry coupled with thermodifferential analysis, scanning electron microscopy for morphological characterization of grains boundary and chemical elementary analysis (ICP) for composition characterization of intergranular phase. The results show that agglomeration is affected by sodium silicate concentration and temperature, the higher the sodium silicate concentration and/or the temperature the stronger is the bonding between grain of sand.

CJ-2:L04 **Effect of Alkaline Earth Oxide on Firing Behaviour of Single Fired Wall Tile Bodies**
Ozgur Cengiz[1]*, Alpagut Kara[1, 2], [1]Dept. of Material Science and Engineering, Anadolu University, Eskisehir, Turkey; [2]Ceramic Research Center, Eskisehir, Turkey

In the production of ceramic wall tiles, fast firing process requires a careful attention with regard to the selection of raw materials. The aim of this study was to determine the effects of alkaline earth oxides on firing behaviour of single-fired wall tile bodies. Several body formulations containing different amounts of MgO and CaO were prepared and fired under laboratory and industrial conditions. The sintering behaviour of the representative bodies were evaluated using a double beam non-contact optical dilatometer (ODHT). The thermal properties were characterised by TG-DTA. The phase and microstructural analyses were carried out by XRD and SEM, respectively. The results show that an optimum combination of the mentioned earth oxides has the potential to give improved technological properties under fast firing conditions.

CJ-2:IL05 **Innovative Use of Industrial Solid Waste in Silicate Ceramics**
Swapan Kumar Das, Central Glass & Ceramic Research Institute (Council of Scientific & Industrial Research), Kolkata, India

Newer materials are now being developed from industrial solid wastes considering the increased worldwide concern for environmental protection, growing economical constraints and depletion of natural resources. The paper deals with four different types of industrial solid wastes viz., Fly ash, Blast Furnace (BF) and Electric Arc Furnace (EAF) slag and iron ore tailing. After detail characterization of the above four wastes, it was observed that all these materials are qualified for use in silicate ceramics particularly for wall & floor tiles, roofing tiles, bricks & pavement blocks. It was observed that Fly ash incorporated composition reaches its standard porcelain microstructure at lower temperature (1200 °C). Partial substitution of felsper by BF slag in a normal porcelain composition enhances the densification & strength at 1200 °C. Distinct changes in microstructure show gradual disappearance of needle shaped mullite crystals & reduction of quartz grain to a certain level followed by appearance of anorthite phase. A composition prepared with EAF slag vitrified at 1140 °C. In another study it was observed that bricks and blocks prepared from a mix of iron ore tailing and clay can be fired at 850 to 900 °C to achieve adequate properties. The paper highlights the scientific findings, microstructure-property- performance relationship, techo-economic advantages and prospect of such new development in the field of silicate ceramics where industrial solid wastes can be judiciously utilized as one of the raw materials.

CJ-2:IL06 **Lightweight Aggregate Processed from Waste Materials**
V. Ducman*, ZAG Ljubljana, Ljubljana, Slovenia; B. Mirtic, NTF, Ljubljana, Slovenia

According to the definition given in the standard EN 13055-1, lightweight aggregate (LWA) is an aggregate with a density of maximum 2 g/cm3. LWAs instead of conventional aggregates are used for two main reasons; they decrease the deadweight of the structures and /or increase their thermal and/or acoustic insulation properties. In the present research, potential use of waste glass, silica sludge, paper mud, paper sludge and polishing residue for the production of lightweight aggregates has been studied on laboratory scale. There are two different mechanisms active in the process of LWA production; the first one is burning out of organic residue in clay matrix, resulting in porous structure. The second mechanism is a foaming process, applicable to glass matrix where a selected foaming agent degasses at elevated temperature, and the resulting gasses remain trapped in the glassy structure. In the presented case, paper mud served as pore-forming agent whereas MnO2 and SiC were added as foaming agents. It was confirmed that selected waste materials can serve as raw materials for the production of LWAs. Depending on the pore forming, foaming agents and regime of firing lightweight aggregate with densities between 0.2 and 1.8 g/cm3 were obtained and analyzed.

CJ-2:L07 **Development of Photochromic Coatings on Ceramic Tiles**
B. Atay[1, 2]*, M. Gurbuz[1], A. Kucuk[2], A. Dogan[1, 3], [1]Anadolu University, Dept. of Material Science and Eng., Eskisehir, Turkey; [2]Kaleseramik Canakkale Kalebodur Seramik Sanayi A.S., Can-Canakkale, Turkey; [3]Advanced Technologies Reseach Center (ITAB), Anadolu Univesity, Eskisehir, Turkey

Photochromic materials are sensitive to light when such a material exposed to the sunlight or UV irradiation, it can change color very quickly and turn back to its original uncolored form by removing light resource. Photochromic powder at different ratios in polymeric gel were prepared and coated on ceramic surfaces by using spray technique. This coating technique provided to form homogeneous layer structure on surface. By using polymeric gel, photochromic coatings formed at low temperatures with good adhesion. After heat treatment fast response photochromic coatings were achieved. Surface morphology of coatings on ceramic surfaces were investigated by Scanning Electron Microscopy (SEM), the photochromic effect and optical characterization of coatings were analysed by using Minolta 3600-d spectrophotometer.

CJ-2:IL09 **Fracture Propagation in Porcelain Tiles During Cooling**
V. Cantavella*, E. Sánchez, E. Bannier, F. Gilabert, Instituto de Tecnología Cerámica (ITC), Asociación de Investigación de las Industrias Cerámicas (AICE), Universitat Jaume I, Castellón, Spain

During the cooling of glass-ceramic materials, micro- and macroscopic stresses develop and microstructural damage occurs, which affect mechanical properties. In materials of the porcelain tile type, such behaviour is complex because several crystalline phases (quartz, albite, and mullite) are found together and the matrix, of a glassy nature, is heterogeneous. A study has therefore been undertaken, using a homogeneous matrix, prepared by fusing a mixture of oxides of the system SiO2-Al2O3-Na2O-K2O. The glass obtained by fusion was milled, and quartz of different particle size was added in varying quantities. Test pieces were then fired at maximum densification temperature and cooled according to the cycles: S: Slow cooling (inside the kiln) FH: Fast cooling to 600 °C and slow cooling from this temperature on FL: Slow cooling to 600 °C and fast cooling from this temperature on

Bending strength, modulus of elasticity, toughness, microcrack size, and macroscopic residual stresses were determined. The residual stresses were basically generated in FH cooling and a model was applied, developed in previous studies by the authors, which predicted the evolution of stresses during cooling. This model was used to relate microstructural damage to the cooling rate.

CJ-2:IL10 **Glassceramics from Vitreous and Ceramic Wastes**

J.Ma. Rincón, Grupo de Materiales Vítreos y Cerámicos, Instituto E. Torroja de Ciencias de la Construcción, CSIC, Madrid, Spain

The necessity and advantages of recycling of wastes with vitreous and ceramics nature, that is basically from construction and demolition (RCD) of buildings, as well as from electronic wastes and manufacture of different production lines are discussed and analyzed. From the life cycle of application of the construction materials, revision of work carried out in the Torroja Institute from different research groups and own research there are showed and discussed the technical as well as scientific results to obtain new glasses, glass-ceramics and even porcelainized stoneware for construction applications.

CJ-2:L11 **Comparison of Weibull Modulus of Aluminosilicate Ceramics Sintered at Various Temperatures**

D.A. Papargyris , A.D. Papargyris*, General Department of Applied Sciences, Laboratory of Materials Technology, Technological & Educational Institute of Larissa, Larissa, Nea Ktiria, Greece

The observed wide scatter in ceramic mechanical strength, resulting in low reliability and high inconsistency of design strength data, is due mainly to inherent micro and macrostructural chemical inhomogeneity and the presence of microcracks with various orientations, a large range of flaw sizes and the residual stresses arising from anisotropic contraction during sintering and cooling. These characteristics make, the use of statistical analysis functions in order to get meaningful results, vital. Stochastic analysis of fracture behaviour under three point bending of alumonosilicate ceramics usually is performed with the use of the empirical in nature Weibull function which is based on the weakest link theory (WLT) (i.e the fracture is attributed to the weakest flaw when the local stress reaches the critical fracture value). In the present work three different formulations of aluminosilicate ceramics differing in silica/alumina content with or without significant presence of other oxides, where mechanically tested and their Weibull modulus (shape parameter) m, estimated from the slope of the linear form of the Weibull function, were compared and discussed with relation to their structure and MOR results.

Session CJ-3
Nanotechnology and Advanced Solutions in Silicate Ceramics

CJ-3:IL01 **Development of New VOC Removal Composite Catalyst Using Silicate Honeycomb Substrate**

Masakuni Ozawa, Ceramic Research Laboratory, Nagoya Institute of Technology, Tajimi, Gifu, Japan

The catalysts for exhaust treatment and VOC (volatile organic compound) removal have been important for controlling of air pollution so far. In the application for automotive exhaust, the combination of honeycomb-type ceramic substrate and precious metal catalyst is widely used as a complete exhaust purifying process device. For ordinary use of catalyst, the honeycomb substrate is also useful, however it is rare that non-precious metal catalyst is combined on the ceramic substrate, because the heat stability is not so established. Also, abnormal combustion phenomena in catalyst often resulted in degradation of catalytic performance. In this work, we have developed a new VOC removal ceramic composite catalyst using nano-particulate ceramic composition, which is combined with silicate honeycomb substrate. The microstructure development of substrate and catalyst layer via heat processing are examined and controlled for precise ceramic parts with catalytic performance. Also, the VOC removal property is demonstrated with several composition of catalyst supported by a substrate. Work supported by City-area project Western Tono “Development of new industry involving environmental friendly ceramics” in Ministry of Education, Culture, Sports, Science and Technology of Japan government.

CJ-3:IL02 **Testing of Photocatalytic Activity of Self-cleaning Surfaces**

Urh Cernigoj, Marko Kete, Urska Lavrencic Stangar*, Lab. for Environmental Research, University of Nova Gorica, Nova Gorica, Slovenia

Due to relatively successful application of TiO2 photocatalysis in the field of self-cleaning surfaces, a reliable and appropriate quantitative method for determining the self-cleaning efficiency of the products (photocatalyst films on different supports) should be widely recognized and established. Currently, the two standard methods are based on photobleaching of methylene blue aqueous solution in contact with thin solid catalyst layer, and on photodegradation of a solid fatty deposit (e.g. stearic acid) over catalyst layer. The first one is focused on an aqueous-solid system and as such it is not the most appropriate one for characterization of self-cleaning surfaces, where solid-solid and solid-air interfaces dominate. The second method (mineralization of a fatty acid) suffers from the slow oxidation (degradation) process of a solid fatty deposit, which is usually followed indirectly by water contact angle (CA) measurements, or by FT-IR analysis. Another method proposed recently is based on the entrapment of an organic dye in a solid polymer matrix deposited over the photocatalyst layer. Upon illumination, the dye (e.g. resazurin) is reduced by the photogenerated electrons to the form of a different colour or to the bleached form. This method is excellent from the qualitative point of view because one can easily observe colour changes of a fast reduction process, but it does not rely directly on a photocatalytic oxidation process (usually taking place in the destruction of organic pollutant under aerobic conditions) and a dye layer over the photocatalyst surface may represent a screen for the photocatalyst. A new method for determination of self-cleaning activity of photocatalytic surfaces was developed in our laboratory. It is based on the deposition of a transparent solid layer comprising terephthalic acid over the photocatalytic surface. When such a system is irradiated, among the other degradation products also a hydroxyterephthalic acid is formed due to a reaction between photoexcited TiO2 and terephthalic acid. Hydroxyterephthalic acid is a highly fluorescent molecule and can be easily detected by HPLC-FLD or spectrofluorimeter. This direct method of following the formation of an oxidation product quantitatively was found to be accurate, highly sensitive and reproducible, therefore it represents a promising option to be considered in standardization efforts in the field of photocatalysis. Many different samples were tested using this method and the standard one based on photodegradation of a solid fatty deposit over the catalyst layer. With regard to the sample (substrate) type, the focus will be given to the self-cleaning ceramic tiles coated in the laboratory with TiO2-SiO2 thin films or commercial ones. In case of self-cleaning ceramics and some other sample types, the advantages of the new method over standard methods will be highlighted and critically evaluated.

CJ-3:L03 **High Temperature Structural Stabilisation of Turkish Sepiolites**

I. Kara*, A. Ozcan, Anadolu University, Eskisehir, Turkey; S. Akar, Eskisehir Osmangazi University, Eskisehir, Turkey

Sepiolite is a layered clay mineral which has a chemical formula of $Si12Mg8O30(OH)4(H2O)4.8H2O$. It has alternating blocks and molecular-sized channels in its structure. The channels have the dimension of 0.37 x 1.06 nm and filled with zeolitic water. When sepiolite is heated, firstly zeolitic water is removed followed by the removal of coordination water. With the progress of the removal of coordination water, the structure of sepiolite collapses, causing closure of the channels. However, it is possible to stabilise the structure of sepiolite even after the removal of coordination water by acid treatment before calcination. In this study, sepiolite is treated by HCl with different molarity and at different times in order to partially remove Mg atoms from sepiolite structure. The effect of acid concentration on the amount of Mg removed was determined by x-ray flouresence. Sepiolite with different amount of Mg removed was calcined up to 600 °C and its structural stability with calcination temperature was followed by x-ray diffraction. Correlation was made between the amount of Mg removed and the structural stability of sepiolite and the best acid treatment condition was determined as the best structural stability with the minimum amount of Mg removed.

CJ-3:L04 **Microwave-assisted Green Synthesis of Noble Metal Nanoparticles**

M. Blosi*, M. Dondi, Istec-CNR Institute of Science and Technology for Ceramics, National Research Council, Faenza, Italy; S. Albonetti, F. Gatti, Department of Industrial Chemistry and Materials, University of Bologna, Bologna, Italy; G. Baldi, CERICOL Colorobbia Research Centre, Sovigliana Vinci, Italy

A green route to the microwave-assisted synthesis of Au, Ag, Cu and bimetallic Au-Ag nanosuspensions has been developed in the light of the large scale production of the studied sols. Metal aqueous colloidal nanoparticles, with high concentration (ranging from 10-2 to 3·10-1 mol/l) and long time stability (12 months) have been achieved by a patented process[1]. The method provides metal nanoparticles, as core-shell structures (Au-Ag) too, through the reduction of metal salts in an aqueous medium. Particle size-control and colloidal stability are achieved by optimizing the reaction, combined with microwave heating, that ensures some advantages over conventional methods. ICP analysis, performed on the unreacted cations, shows high reaction yields; moreover electron microscopy (STEM, TEM) and dynamic light scattering (DLS) confirm the mono-dispersed size distribution of nanoparticles with a mean diameter ranging from 10 to 80 nm. Finally, surface plasmon resonance (SPR) was monitored by UV-VIS spectroscopy. All the optimized suspensions have been tested as ceramic inks for ink jet printing technology, and the colour changes induced by Au-Ag bimetallic structures have been explored. Moreover, silver nanosuspensions show both on ceramic tiles and glasses good antibacterial activity.

[1] *M. Blosi, S. Albonetti, M. Dondi, G. Baldi, A. Barzanti, Patent: FI2009A000034 (2009)*

CJ-3:IL05 Nano-sized Coatings Modification Applied in Microfiltration Membrane Technology

Jian-er Zhou*, Qibing Chang, Yongqing Wang, Xuebing Hu, Xiaozhen Zhang, Jingdezhen Ceramic Institute, Jingdezhen, P.R. China

Nano-sized coatings with super-hydrophilic/hydrophobic properties are generally deposited on smooth substrates. The authors aim at improving of the filtration efficiency and selectivity by modification of the porous inorganic membranes through depositing a very thin nano-sized coating on the membrane channels' surface. It is found that the filtration characteristics are distinctively varied by the homogeneous nano-sized coating that obtained by a homogeneous precipitation or an in-situ hydrolysis method. (1) The pure water permeation is increased by 20%~50% despite of the decrease of the mean pore size of the membrane. It is a ubiquitous phenomenon caused by the introduction of the nano-sized coating, and it can be attributed to the modification of the membrane's morphologies, the surface charge, the roughness, and the water flow behavior on the nano-size coatings surface. (2) And a higher oil-water separation efficiency of 99% is obtained, which is due to the super hydrophilic surface of the nano-sized coatings. The permeate flow of the modified membrane is obviously higher than that of the unmodified one. Specially, the steady flow is reache in a short time (<10 min) and keeps a constant in the remained time. The work shows a good prospect in potential commercial applications.

CJ-3:IL06 Nanostructured Glassy and Ceramic Surfaces: Development of "Active" Materials for an Innovative Approach to Building Industry

Giovanni Baldi*, Andrea Cioni, Valentina Dami, Colorobbia Italia, Sovigliana-Vinci (FI), Italy

There is an increasing interest of the scientific community and industry in the field of healthy and eco-buildings. Nanotechnology meets the efforts in the development of new advanced materials, which can be environmentally sustainable and safe for the consumers. Due to their multi-functional behaviour, nanomaterials are at the basis of a revolutionary technical improvement in buildings. Titanium nano-structured films applied on ceramic and glass surfaces increase drastically the self-cleaning and anti bacterial activity. We can engineer porous substrates to obtain anti-pollution surfaces either for external and internal applications, to help customers in the certification of eco-buildings; CERICOL in particular, has developed a photo-reactor to assess the photo degradation kinetics of NOx and VOC. We have also demonstrated that the use of nano metals, like gold and silver, leads to an anti bacterial action in absence of light, meanwhile anti-scratch and zero-porosity substrates can be obtained thanks to nano zirconium and nano silica suspensions. CERICOL has developed and scaled up "green chemistry" synthesis in liquid media that encourages an easy industrial application on different building substrate as tiles, glass, paints and even plastics, wood etc... The use of different compatible nanomaterials leads to multi-functional nano-structured substrates for buildings with improved features. A careful analysis of risk assessment and of toxicological aspects has been also done in order to evaluate the complete eco-compatibility of this new technology.

CJ-3:L07 Effect of Nanosized TiO2 on Nucleation and Growth of Cristobalite in Sintered Fused Silica Cores for Investment Casting

G. Casarano, A. Licciulli, Università del Salento, Dipartimento Ingegneria dell'Innovazione, Lecce, Italy; A. Chiechi*, D. Diso, Salentec Advanced Technologies, Cavallino (LE), Italy; P. Bene, D. Bardaro, Centro di Progettazione Design e Tecnologie dei Materiali, Brindisi, Italy; M. Di Foggia, Europea Microfusioni Aerospaziali Spa, Morra de Sanctis (AV), Italy

Sintered fused silica is often used for making sacrificial cores in investment castings of Ni superalloys. Their usage is fundamental in the manufacture of precise superalloy gas turbine components with complex internal cooling passages. In this study SiO2/TiO2/ZrSiO4 mixtures were prepared from fused silica powders with different grain size and zircon and TiO2 content by slip casting method. Green samples were sintered from 1050 °C up to 1350 °C at various soaking time. Thermomechanical and microstructural properties were investigated by three point bending tests, SEM, XRD and Hg porosimetric analysis. The influence of cristobalite content on thermal stability at high temperature was studied by means of an optical dilatometer. TiO2 appears to act as a phase transformation inhibitor reducing the transformation rate of fused silica to cristobalite at high temperatures. A comparison with commercial silica cores made by injection moulding has been performed. Very precise silica prototype cores were obtained by CNC and an investment casting was performed on that.

CJ-3:L08 New Low Temperature Routes For the Preparation of Strontium Orthosilicate Using High Surface Area Mesostructured Silica

Jones Leite Soares, Flavio Maron Vichi*, Institute of Chemistry, University of Sao Paulo, Sao Paulo, Brazil

Strontium orthosilicate is an interesting material due to its possible application in the production of white phosphors and LEDs when doped with Eu(II). Common synthetic routes generally involve the mixing and calcination of strontium carbonate and silica at temperatures as high as 1500 °C, a very energy-intensive process. Alternative lower temperature routes have been hindered by the extremely high thermodynamic stability of strontium carbonate. In this contribution, we report two synthesis of strontium orthosilicate at temperatures which are less than half of the previously reported values. Route 1 couples a molten-salt (NaCl-KCl) route with the use of mesostructured MCM-41-type silica and strontium nitrate. X-ray diffraction confirms the formation of the beta-strontium orthosilicate at 700 °C. In route 2, the synthesis was carried out in molten sodium nitrate at 600 °C, but in this case the product is alfa-strontium orthosilicate as a single phase. The material prepared via route 1 has a surface area of 12 m2/g and a very broad pore diameter distribution, spread over the interval 2-21 nm, whereas the material prepared via route 2 has a lower surface area (9 m2/g), but shows a much narrower pore size distribution, centered between 3 and 5 nm.

Session CJ-4

Decoration, Colour and Design of Silicate Ceramics

CJ-4:IL01 Digital Decoration of Ceramic Tiles: Current Situation and Outlook

M. Dondi, CNR-ISTEC, Institute of Science and Technology of Ceramic Materials, Faenza, Italy

Decoration is the sector of the tilemaking industry where innovation is faster, particularly due to the recent introduction of the ink-jet printing technology. Current situation and the most recent developments of digital decoration in the ceramic tile manufacturing are reviewed. Novel chances of decorative expression, made possible by ink-jet printing and other digital techniques, are illustrated. Advantages and limits of digital technologies are throroughfully revised. The problems encountered during the transfer process of digital technology to the ceramic sector are discussed, along with the technological solutions adopted, with special emphasis on: digital design; ink-jet printers; behaviour of printing heads; requirements and characteristics of inks for digital printing; type and performance of pigments used in ink-jet decoration; interactions of inks with ceramic substrates. Open questions are posed in order to highlight key-points needing further development and to address future perspectives of digital decoration in tilemaking.

CJ-4:IL02 Innovations and New Trends in Ceramic Tile Decoration

Arnaldo Moreno Berto, Instituto de Tecnología Cerámica (ITC), Asociación de Investigación de las Industrias Cerámicas (AICE), Universitat Jaume I, Castellón, Spain

Ceramic tile decoration techniques have undergone major changes during the last years, as a cosequence of a number of facts of different nature. On one side, the need to launch products with new aesthetic features leading to widen the existing range, has facilitated the appearance of new decoration techniques allowing to attain effects hard to achieve not long ago. On the other side, environmental constraints have also contributed to develop new decoration systems, as well as to improve the existing ones, with a view to making them cleaner or to reducing wastes derived from their utilization (waste waters, sludges, etc). Some of these new techniques are based on physical principles quite different from those used in traditional ones and, in other cases, are more or less relevant variations of them. The goal of this paper is to review the last innovations in ceramic tile decoration techniques, covering not only the most spread ones (rotogravure, flexography, ink jet printing) but also some others with a strong potential to provide tile surfaces with new finishes and aesthetic features, such as Physical Vapour Deposition or Laser treatment. A prospecive of the future trends in this field will be presented at the end of the paper too.

CJ-4:L03 **CoAl2O4 Nanopigment Obtained by Combustion Synthesis**

F. Bondioli, Sh. Salem*, S.H. Jazayeri, A. Allahverdi, M. Shirvani, Department of Material and Environmental Engineering, University of Modena and Reggio Emilia, Modena, Italy; School of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran

In this research, solution-based combustion synthesis was applied to prepare the spinel $CoAl_2O_4$ pigment from precursor solution of $Al(NO_3)_3.9H_2O$ and glycine. Effect of pH values (2.5, 7, 10.5), the molar ratio of fuel to nitrates in the precursor solutions (1.5, 2) and the subsequent calcinations temperature (600, 800, 1000, 1200 °C) on the powder characteristics were described. Gel formation, morphologies, specific surface area and colour of the powder were characterized using DTA/TG, XRD, TEM, BET and UV-Vis. Also quantitative analysis of the obtained samples was performed by the Rietveld-R.I.R. method. The results indicate that the crystalline spinel $CoAl_2O_4$ was formed at all different Gl/NO_3^- molar ratios, pH and temperatures and higher temperature promote the increase of the crystallite size. According to TEM figures most of the particles calcined at 800 and 1000 °C has sizes less than 50 and 100 nm respectively. Corresponding to results of BET experiment, specific surface area has its maximum values at $pH = 7$ and decreases with increasing of temperature. The results of UV-Vis shows that the powders calcined at 600 °C are not blue and when temperature increases the amount of b* decreases. Finally the applicability in commercial frits for ceramic glaze was successfully tested.

CJ-4:IL04 **Development of New Ceramic Dyes**

G. Monrós, Dpt. Química Inorgànica i Orgànica, Universitat Jaume I, Castellón, Spain

Research on new ceramic dyes is addressed to obtain best pigmenting materials in order to reach higher thermal stability (e.g. for porcelainised stoneware) than classical pigments, higher chemical stability towards the coloured matrix or low toxicity in order to satisfy health and environmental requirements. The earlier developments on the research in new ceramic pigments based on new crystal structures (e.g. phosphates, hexaaluminates, neodymiates, fergusonite, titanite, pseudobrookite), new chromophores (e.g. ruthenium, bismuth, vanadium and rare earth ions.), or new methods of preparation (e.g. citrate route, spray drying, aquo-organic coprecipitation, polyol route.) are discussed in this communication.

CJ-4:IL05 **New nMetal-sepiolite Bioactive Nanocomposites as a Special Effects Pigments (Colors and Shining) for Decoration of Ceramic Tiles**

José S. Moya, ICMM-CSIC Cantoblanco, Madrid, Spain

In the present investigation we have obtained metalized glazes by a conventional fast firing bottom-up route starting from a silica-rich fibres (sepiolite) containing monodispersed metallic nanoparticles (Cu, Fe, Au, Ag). These fibres have the capability to keep the metallic nanoparticles disperse in the glaze avoiding its aggregation during the conventional fast-firing step. The main characteristics of these glazes such as: microstructure, optical properties and biocide properties will be reported and discussed.

CJ-4:IL06 **Novel Ceramic Pigments Based on Industrial Wastes**

W. Hajjaji[1], G. Costa[2], M.J. Ribeiro[2], M.P. Seabra[1], J.A. Labrincha[1]*, [1]Ceramics and Glass Eng. Dept., CICECO, University of Aveiro, Aveiro, Portugal; [2]ESTG, Polytechnic Institute of Viana do Castelo, Viana do Castelo, Portugal

We report the preparation of ceramic pigments using industrial wastes as primary sources. Al-rich sludge generated in the wastewater treatment unit of an anodising or surface coating industrial plant, a galvanizing sludge from the Cr/Ni plating process, foundry sand, and marble sawing sludge are combined to formulate distinct pigment structures by the solid state reaction method. In particular, a black spinel and a novel blue pigment based on the hibonite structure will be detailed. The pigments were fully characterised and then were tested in a standard ceramic glaze after. Typical working conditions and colour development are fully described.

Poster Presentations

CJ:P01 **Almost Complete Nitridation of Mesoporous Silica to Mesoporous Silicon (Oxy)Nitride with Ammonia**

Fumitaka Hayashi, Masakazu Iwamoto*, Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan

Mesoporous silicon oxynitride (MSON) and nitride (MSN) were prepared from various mesoporous silica using a plug flow reactor instead of a boat reactor. At first, nitridation was examined as a function of reaction temperature, time, sample weight, and flow rate of ammonia. The nitridation rates were slow at 973-1073 K, and increased at or above 1173 K. The appropriate nitridation temperature was 1273 K because 1323 K was too high to maintain the pore structure. The maximum contents of nitrogen were 35-38 wt% at 1273 K, which correspond to 90-95% of that of Si3N4, and were much greater than those of previous reports. The amount of NH3 supplied to mesoporous silica is the significant factor to determine the degree of nitridation. The present nitridation technique could be applied to various types of mesoporous silica, indicating that nitridation reaction is almost independent of the pore size and the structure. In contrast, silica gel was difficult to be nitrided and its surface area reduced drastically. The XRD, N2 adsorption, and SEM/TEM measurements of MSONs indicated that the pore structures were not changed after the nitridation though the lattice constants and the pore diameters decreased and the wall thicknesses increased.

CJ:P02 **Microstructural Evolution of Fast Firing Floor Tiles Produced by Experimental Design Method**

Ahu Koda*, Gursoy Arslan, Anadolu University, Material Science and Engineering Department, Eskisehir, Turkey

In this work, as a part of an extended study where previously published set of experiments were designed as 2132 mixed-level factorial design approach used and individual effects of the main four factors and their interactions determined. Detailed investigation microstructural evolution of fast firing floor tiles were carried out using X-ray diffraction (XRD) and scanning electron microscopy (SEM) in combination with energy dispersive spectroscopy (EDX). The obtained data was also correlated with some of technological properties of the selected bodies. The results were compared with those already presented in the relevant literature.

CJ:P03 **Use of Spodumene in Porcelain Stoneware Formulations**

T. Aydin*, Dept. of Material Science and Engineering, Anadolu University, Material Science and Engineering Dept., Eskisehir, Turkey; A. Kara, Ceramic Research Center, Eskisehir, Turkey

Lithium aluminosilicates, such as spodumene, have been used as raw materials in the production of thermal shock resistant whiteware and sanitaryware. The presence of spodumene causes enhancement of mullitization and imparts better physical and mechanical properties to ceramics. In this study, the influence of Li2O-content on the properties of a standard porcelain stoneware body was investigated. Sodium feldspar was replaced by the spodumene in varying amounts (up to 4 wt. %). The results showed a significant microstructural improvement, the presence of spodumene which, during firing, allows the development of a low viscosity liquid phase with a decrease of both closed porosity and average pore size, also with increasing bulk density and stain resistance.

CJ:P06 **Fast Firing of Glazed Tiles Containing Paper Mill Sludge and Glass Cullet**

G. Tonello*, E. Furlani, S. Maschio, D. Minichelli, S. Bruckner, Università di Udine, Dipartimento di Scienze e Tecnologie Chimiche, Udine, Italy; E. Lucchini, Università di Trieste, Dipartimento di Ingegneria dei Materiali e delle Risorse Naturali, Trieste, Italy

The present paper reports on the results of some experiments on the progress of a previous research and describes the production, in single fast firing, of tiles containing 30% wt of a natural red clay and a mixture of 42 wt % of paper mill sludge and 28 wt % of glass cullet which were coated with a commercial “matt white” glaze. Fired materials were characterized as a function of the top temperature (1090 or 1140 °C) reached during the fast sintering process made in an industrial roller kiln. It is observed that tiles fired at 1090 °C display the best overall performances since the matt glaze well covers the substrate concurring to mantain in line with the official standard for production mechanical and physical properties of the tiles.

CJ:P08 **Influence of Clayey Material on the Sintering Behaviour of Ceramics Containing Paper Sludge and Glass Cullet**

E. Furlani*, S. Maschio, G. Tonello, E. Aneggi, D. Minichelli, S. Bruckner, Università di Udine, Dipartimento di Scienze e Tecnologie Chimiche, Udine, Italy; E. Lucchini, Università di Trieste, Dipartimento di Ingegneria dei Materiali e delle Risorse Naturali, Trieste, Italy

In the present work we have studied the sintering behaviour of several ceramics materials prepared using a selected mixture of incinerated paper mill sludge and glass cullet which was blended with 10, 20, 30 and 40 wt% of some natural clayey materials. Three natural commercial product were used: a red quartzitic clay, a yellow quartzitic clay and a kaolin. The blended mixtures of powders were pressed into specimens and then fired at different temperatures for 1 h. The resulting materials were characterized by water absorption, shrinkage, hardness, bending rupture strength, crystallographic composition and microstructure. It was demonstrated that all the materials made using kaolin reach good properties when fired at any temperature between 1040 and 1140 °C whereas the optimal sintering temperatures of the samples prepared using red of yellow clay are function of their specific composition.

CJ:P10 **Development of Synthetic Soapstone from Natural Soapstone Powder and Debris**

C.E.S. Amorim*, M.G.A. Ranieri, R.P. Mota, M.A. Algatti, FEG-DFQ-UNESP, Campus de Guaratinguetá, Guaratinguetá, SP, Brazil; E. Campos, Escola de Especialistas da Aeronáutica, Guaratinguetá, SP, Brazil; F.C.L. Melo, AMR/IAE/CTA, Sao José dos Campos, SP, Brazil

The region surrounding the city of Ouro Preto, MG state, Brazil, has a huge tradition on producing industrial and handicraft objects from natural soapstone. This tradition started on the 18th century with the Aleijadinho’s sculptures that are considered by UNESCO as a mankind patrimony. Nowadays two main drawbacks may be identified concerning the production of soapstone goods in that region. The first one is the economical situation of the small handcrafters and the second one is the illegal drop of soapstone powder and debris at streamlets and lakes. This paper deals with the production of synthetic soapstone using the soapstone powder resulting from the industrial activity. The process consists in uniaxial pressing of soapstone powder with water soluble additives. The two criteria chosen for synthetic soapstone evaluation were: The performance test following the handcrafter’s point of view and laboratory tests like roughness, wettability and mechanical resistance. Obtained results showed that the flexion mechanical resistance is quite similar to the natural soapstone and that the homogeneity is higher than the natural one. Contact angle measurements showed that the hydrophobic character of the natural soapstone was kept on the synthetic one.

CJ:P11 **Determining the Chemical Composition of Glass Phases in Sanitarywares by Quantititive X-ray Diffraction Analysis**

Hasan Sari*, Semra Kurama, Anadolu University, Department of Materials Science and Engineering, Eskisehir, Turkey

Sanitarywares consist of crystalline phases that are surrounded by glassy phases. The glassy phase viscosity affects the firing conditions in sanitaryware bodies. Therefore, the amount of glassy phase plays an important role on determining the composition of glassy phases. In this study, crystalline phases were determined as quantitatively by using the ratio of slopes method. For that reason, X-ray diffraction (XRD) analyses were used in calculation of glassy phase composition in standard sanitaryware body. The results are also contributed to enhanced new sanitaryware compositions.

CJ:P12 **Research-studies on Hard Porcelain Glazes**

A. Goleanu, S.C. Apulum S.A., Alba Iulia, Romania

The present work aims to study the influences of the composition and processing of the glaze on the quality of the surface and the occurrence of various defects (chiefly bubble defects - pinholes), with the final purpose to obtain a defect-free glaze. Several high temperature porcelain glaze compositions have been designed, using different selected raw materials. The glazes have been fired onto products made of hard porcelain bodies, in fast firing processes and they were then subjected to visual inspection of the outward appearance and surface qualities. The thermal behaviour of the glazes was investigated through: thermogravimetric (TG) and differential thermal (DTA) analyses; dilatometric analysis; softening tests performed using the heating microscope; estimation of the viscosity / variation in viscosity as function of temperature; measurements / calculation of the surface tension at a specified high temperature. A study of the phase composition and microstructure of the test glazed specimens was done by XRD and SEM - EDX investigations. Based on the obtained results, several conclusions were drawn regarding the way of reduction or, preferably, elimination of defects in glazes.

CJ:P13 **Structural Evolution and Mechanical Properties of Silicate Ceramics Sintered with BaF2 and CaF2 Nanoparticles**

R. Torres, H. Valle, Mexichem Fluor; L. Flores, Facultad de Quimica-UASLP; O. Dominguez*, IM-UASLP, San Luis Potosi, Mexico

The present work presents preliminary results concerning the effect of BaF2 and CaF2 nanoparticles on the sintering behavior of traditional silicate ceramics. The nanoparticles were synthesized using aqueous solutions of Ca2+ and Ba2+ dissolved in water with an organic dispersant and precipitated with KF. The obtained nanoparticles were square-like having a mean length of 25 nm. Two silicate materials were mixed with different amounts of nanometric CaF2 and BaF2 (from 0.25 to 5.0 wt%) and mixtures were milled, pressed and sintered. From sintering experiments, it was observed that small additions of CaF2 and BaF2 nanoparticles in clays could shift the phase transition temperatures to lower values. Specifically, the densification temperature could be reduced by almost 150 °C when 1.5 wt% of CaF2 was incorporated. Besides, adding 1.25% of nanometric BaF2 can achieve that compressive strength augments from 125 to 170 MPa in kaolin based clays sintered at 1200 °C, meaning an improvement of almost 40% in the properties of the final material.

CJ:P14 **Quantitative Infrared Thermography (IRT) and Holographic Interferometry (HI): Nondestructive Testing (NDT) for defects detection in the Silicate Ceramics Industry**

S. Sfarra*, D. Ambrosini, A. Paoletti, D. Paoletti, Department of Mechanical, Management and Energy Engineering (DIMEG), University of L’Aquila, Loc. Monteluco di Roio (AQ), Italy; C. Ibarra-Castanedo, A. Bendada, X. Maldague, Computer Vision and Systems Laboratory, Department of Electrical and Computer Engineering, Laval University, Quebec City, Canada

Ceramics are inorganic materials fabricated by a high-temperature chemical reaction. Most ceramics are oxides, but the term is also used for silicides, nitrides and oxynitrides, hybrids and other inorganic materials. It is convenient to consider ceramics that are essentially silicates, called traditional ceramics, separately from all of the others. In the ceramic industry testing systems are seldom employed for detecting on-line the presence of defects in ceramic tiles. Defects in the ceramic body are usually originated during the pressing stage due to the incorrect use of process parameters or to the improper selection of raw materials. These defects are generally characterized by the inclusion of heterogeneous materials or agglomerates, which decreases the structural strength jeopardizing the final quality of the produced piece. Disagreeable repercussions on the sale market, especially on higher-quality ceramics such as porcelain, are characterized by the lack of specific nondestructive testing (NDT) techniques that “certify”, pre-emptive, the quality of the produced piece. The integration of IRT and HI for the NDT of a green ceramic tile with both fabricated and real defects (cracks caused by the natural shrinkage process), allowed us to produce a clear “defects map”.

CJ:P15 **Visible and Infra-red Reflectance of Several Typical Japanese Glazes for Roof Tiles and Wall Tiles**

T. Sugiyama*, H. Kakiuchida, M. Ohashi, National Institute of Advanced Industrial Science and Technology, Materials Research Institute for Sustainable Development, Nagoya, Japan

Higher reflectance coatings against sun light are effective in mitigating heat-island phenomenon. Covering the surface of ground or outside of buildings with such high reflectance coatings has attracted attention because of its high cost performance. Companies producing Japanese roofing tiles or wall tiles are recently trying to develop high reflectance glaze for their products. However, there are less data of infrared reflectance on pottery glazes, while we have enormous data on their visible reflectance measured in studying coloration of glaze. Though optical properties of simple glass and ceramics have been well studied, pottery glazes are complex glass-crystalline micro-composites. The pottery glazes sometimes have heterogeneous structures caused by phase separation, crystallization in base glass, oriented crystallization on surface, and so on, which are considered to affect infrared reflection. In this paper, several kinds of Japanese typical glazes are characterized from the point of view of the visible and infra-red spectral reflectance, and their improvement is discussed.

CJ:P16 Colour Properties of Y2O3-Al2O3-Cr2O3 Pigments as a Result of Precursors Morphology

Ewa Stobierska, Miroslaw M. Bucko, Jerzy Lis, Katarzyna Kuzminska*, AGH - University of Science and Technology, Faculty of Materials Science and Ceramics, Cracow, Poland

Double yttrium-aluminium oxide of perovskite structure (YAP) doped with chromium(III) ions seems to be promising material for red pigments for gres porcellanato ceramic masses. The aim of the present paper is to examine an influence of precursor morphology on colour properties of the pigments. Two kinds of chromium oxide and aluminium hydroxide powders were used. The average grain size of the fine chromia powder was about 1µm whereas the one of the coarse powder was about 50 µm. The fine Al(OH)3 powder was amorphous with D50 = 3.5 µm and the coarse one was crystalline gibbsite with D50 = 35 µm. It was stated that grain size of Cr2O3 did not influence neither phase composition nor colour properties of the powders whereas using of aluminium hydroxide powders of different morphology led to substantial differences in phase composition. Using of coarse crystalline aluminium hydroxide powder caused formation of over 95 wgt.% of YAP phase whereas the pigments prepared with amorphous aluminium hydroxide were composed of YAP (~65%) and Y2Al4O9 (YAM). In the later case, increase of calcination temperature caused formation of yttrium aluminium garnet phase (YAG) instead of YAM phase. The differences in phase compositions expressed differences in colour properties of the respective pigments.

CJ:P17 New Red Chromium-calcium Titanate Red Ceramic Pigment

C. Gargori*, R. Galindo, M. Llusar, S. Cerro, A. García, G. Monrós, Dpt. Química Inorganica i Organica, Universitat Jaume I, Campus Riu Sec, Castellón, Spain

Synthesis and characterization of a new chromium-calcium titanate red ceramic pigment is described in this communication. The solid solution of chromium(IV) in calcium titanate is calculated in order to obtain red-brown colours in a CaO-ZnO-SiO2 transparent glaze used for ceramic tiles avoiding green tonalities. XRD, UV-Vis-NIR spectroscopy and CIE-L*a*b* techniques of characterization have been employed. The L*a*b* valour of the pigment with 0,1 mol/mol of chromium fired at 1100 °C with a soaking time of 3 hours and 5% weight added to the transparent glaze is 42,7/16,8/20,7.

G. Pfaff, Synthesis of Calcium Titanate Powders by Sol-Gel Process, Chem. Mater. 1994,6,58-62; I.V. Pischc, E.V. Radion, Synthesis of pigments base don perovskite, Glass and Ceramics, 1998, 55, 290-291

CJ:P18 The Effect of Ferrochromium Fly Ash as a Pigment on Wall Tile Glaze

Zahide Bayer*, Nuran Ay, Anadolu University, Faculty of Engineering and Architecture, Department of Materials Science and Engineering, Iki Eylul Campus, Eskisehir, Turkey

Fly ash, is a waste of ferrochromium production which contains high amount of Cr_2O_3 and Fe_2O_3. In this study, fly ash was used as a colorant for wall tile glaze. Pigments were produced by using Cr_2O_3, Fe_2O_3, CoO and fly ash, added to glaze composition at different ratios (wt. 1-5 %). Glazes were applied on ceramic tiles and fired at 1145 °C/ 30 min. Glazed tiles were analysed by using Harkort, autoclave and color measurement tests. As a result, by increasing of fly ash content, the color of glaze changed from brown to grey. It is observed that Harkort and autoclave tests of glazed tiles provide the convenience of the standards. These results as a whole suggest that the use of fly ash in wall tile glaze constitutes a potential means of adding value.

CJ:P21 Crystallisation of Gahnit in CMAS Glass Forming System. Mechanism and Kinetics of the Process

Daniela Herman*, Tomasz Okupski, Koszalin University of Technology, Koszalin, Poland

Mechanism of glass-crystalline materials crystallisation from a CMAS Al0,37 B0,35Mg0,02 Zn0,29Ca0,05Si0,78O3 group was tested by DTA method under non-isothermal conditions. In the system under investigation from established chemical constitution the material of diphase mineralogical composition with crystallite precipitations from an island silicate group and the crystalline phase belonging to a group of spinels (ghanit ZnAl2O4) were obtained. The activation energy Ea of the process of crystallisation was determined and the morphology parameter of crystal growth was calculated using Augis-Benett's equation. The activation energy of the material under investigation determined by Kissinger's method was fluctuating within the range from 370 [kJ/mol] to 376 [kJ/mol]. It was revealed that in the system of materials belonging to a CMAS group it was possible to obtain a crystalline phase in the form of gahnit as a result of a controlled process of crystallisation. Due to the presence of a spinel phase the obtained glass-crystalline phase revealed higher mechanical properties (KIc) than the materials from a CMAS group composed of pyroxene crystalline phases typical of this system. The microstructure was analysed by SEM and EDS methods to confirm phase transitions and chemical composition.

Symposium CK

GEOPOLYMERS AND GEOCEMENTS: LOW ENVIRONMENTAL IMPACT CERAMIC MATERIALS

Oral Presentations

Keynote Lecture

CK:KL **Status and Prospects of Research and Application of Alkali-activated Materials**
Pavel V Krivenko, Kiev, Ukraine

Development of alkaline (alkali-activated) cements and concretes is supported by 50 years of theory and practice in this field collected by Ukrainian scientific school, the head of which - Professor V.D.Glukhovsky - was the first who as long as in 1957 put forward an idea of alkaline activation. The paper includes an overview of the state- of- the- art on the alkaline cements and concretes. Above, it covers history of development of the alkaline cements, their classification, terminology, principles of compositional build-up, processes of hydration and hardening, etc. Special attention is paid to aspects of durability, since durability is a key factor in building materials. A theoretical background explaining reasons of excellent durability of the alkaline cements is disclosed and discussed in terms of macro- and microstructure. Facts supporting evidence of exceptional durability of the alkaline cements and concretes are given in the paper together with the results of comparative analysis of the durability of the alkaline cement and OPC concretes.

Session CK-1
Preparation

CK-1:IL01 **Synthesis Routes of Novel Inorganic Polymer and Geopolymer-type Materials**
K.J.D. MacKenzie, MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, New Zealand

”Conventional” synthesis of aluminosilicate inorganic polymers involves reactions under highly alkaline conditions between an alkali silicate solution and a solid aluminosilicate source (often metakaolinite, but not necessarily). Alternative syntheses have been developed that involve precipitation from solution (“soft” chemistry) or solid-state reactions between the starting materials producing hydraulically-active geopolymer precursors. The latter method is particularly appropriate for preparing inorganic polymers of elements such as lithium which are not sufficiently alkaline, or analogues of aluminosilicate geopolymers that are inaccessible by the conventional route. This presentation will discuss the development of these new synthesis routes and their application to the preparation of a number of otherwise inaccessible novel inorganic polymer compounds.

CK-1:IL02 **Preparation of Geopolymeric Materials from Swage Sludge Slag, a Novel Active Filler**
Norio Yamaguchi, Ceramic Research Center of Nagasaki; Ko Ikeda*, Prof. Emeritus of Yamaguchi University, Ube, Japan

Conversion of urban wastes into slag by fusion is becoming popular in Japan in order to elongate the life capacity of discarding sites. On the other hand, recycling of wastes is strongly recommended to realize zero-emission societies. Geopolymer liquor was prepared by mixing 1.69M Na2O.2SiO2 and 10M NaOH solutions in 3 : 1 proportion. Swage sludge slag, SSS, was mixed with coal fly ash, CFA in 25% intervals. Then, the geopolymer liquor was well-mixed in 0.43 W/S. Then, the charge was steam-cured under 60-80 °C-80%RH conditions for up to 24h by casting into prismatic molds having 20x20x80mm dimension. Sufficient handling time over 1h for mixing was available. Obtained monolithic bodies were quite stable in forms showing almost the mold size. The CFA dosage is helpful not only to supplement the amount of SSS but also to improve the mechanical strength. Maximal strength was reached in 6 h steam-curing and further elongation of curing time made the strength decrease. The SEM-EDX analysis showed a vivid incorporation of Al2O3-component into the matrix portions. Incorporation of P2O5- and CaO-components was also clearly detected, which were major constituents of the SSS filler. In addition, high accumulation of SO3-component was noted in presence of CFA filler, explaining highly resistant property to sulfuric acid.

CK-1:IL03 **The Role of Molecular Research in the Commercialization of Geopolymer Concrete in Australia**
J.S.J. van Deventer*, P. Duxson, Zeobond Pty Ltd, Somerton, Victoria, Australia; J.L. Provis, C.E. White, Department of Chemical & Biomolecular Engineering, The University of Melbourne, Victoria, Australia

Geopolymer concrete which is derived from coal fly ash and blast furnace slag activated by alkali has recently been commercialized by Zeobond Pty Ltd in Australia. The product has been well received by the end-user community and regulatory authorities, including applications in structural panels, pedestrian pavements, bridge decks, foundations and retaining walls. The main driver for adoption of this material is the push for low carbon materials. To bring a product to market in this competitive industry requires a strong basis of scientific understanding. In order to produce a practical alkali-activated geopolymer concrete there has been extensive research into both the real-world material and a variety of associated model systems. In this paper, we outline how molecular research on these model systems has contributed to understanding the commercial product. Techniques utilized include density functional modeling, local structure analysis from total scattering, nano-tomography and fluorescence microscopy. Hence, by understanding the mechanisms responsible for the behavior of model systems, and therefore various aspects of the chemistry of geopolymers, especially at the nanoscale, there exists substantial evidence regarding the performance and durability of this new material.

CK-1:L05 **The Incorporation of Gallium Into Inorganic Polymer Structures: Synthesis and Thermal Behaviour**
A.T. Durant*, K.J.D. MacKenzie, Victoria University of Wellington, Wellington, New Zealand

Novel gallium silicate and gallium aluminosilicate inorganic polymers (IPs) were synthesised from mixtures of KGaO2, KAlO2, KOH solutions with silica fume, using a combination of newly developed sol-gel and solid-state techniques. The products of these reactions were studied by XRD, solid-state 27Al, 29Si, 71Ga and 39K MAS-NMR and SEM. The optimal SiO2:(Ga2O3+Al2O3) ratio was found to be 7 and the Ga:Al ratio could range from 100% Ga to 100% Al. The products showed all the characteristics of a true IP, being X-ray amorphous and containing Ga and/or Al in tetrahedral coordination states. 29Si MAS NMR showed the occurrence of Si(3Ga), Si(2Ga), Si(3Al) and Si(2Al) sites. Unreacted silica was also detected in these compounds by 29Si NMR and spherical silica particles were observed by SEM. Heat treatment of gallium silicate, gallium aluminosilicate IPs was monitored by thermal analysis methods (DSC-TGA) which revealed a water loss at 75 °C and 160 °C followed by a phase transition at 950 °C. At this temperature the IPs crystallised to KGaSi2O6 and KAlSi2O6. At 1200 °C the high-temperature products derived from the gallium silicate IPs remained as crystalline KGaSi2O6, while gallium aluminosilicate IPs melted and slumped, losing their shape and becoming X-ray amorphous.

CK-1:L06 **Kinetic Analysis of Processes Underlying Geopolymerization and Gain of Strength**
C. Chen, W. Gong, W. Lutze*, I.L. Pegg, The Catholic University of America, Washington, DC, USA

An analysis has been performed of chemical reactions and rate-limiting steps leading to geopolymerization of fly ashes F. The kinetics of corrosion of the glass phase was studied with and without geopolymerization, depending on the water-to-solid ratio (W/S). Independent of W/S, temperature, and alkali molarity the same rate laws have been identified but their relative significance depends strongly on afore mentioned variables. At W/S>10, a significant fraction of the glass reacts, following a first order rate law, allowing us to evaluate different fly ashes by their composition, which affects their reactivity. Later in the process, gel and then crusts of zeolite form and transport of (most likely) OH- controls a slower reaction progress. At W/S=10 glass dissolution is insignificant. Zeolite does not form. At W/S=0.35, typical of geopolymerization, glass alters by formation of surface and interstitial gel. The transition between two distinct transport processes marks the point at which a geopolymer paste gains mechanical strength. The increase of strength is probably related to a slow change in the chemical composition of interstitial gel. The SiO2/Al2O3 ratio attains that in the glass; R2O/Al2O3 approaches one, i.e. charge balance. All effects will be discussed quantitatively.

CK-1:L07 **Understanding Study of Silicate-based Gel formed during the Setting of Ceramic Materials**

M.T. Tognonvi*, S. Rossignol, J.P. Bonnet, GEMH-ENSCI, Limoges, France; A. Lecomte; SPCTS-ENSCI, Limoges, France; D. Massiot, CEMHTI-CNRS UPR 3079, Orléans cedex, France

Consolidation of cementitious and geopolymer materials involves the formation of silicate-based gel. This in situ mechanism is difficult to identify and to control because it occurs in a complex and evolving system. This study is based on the behaviour of acidified sodium silicate solutions in alkaline medium in order to define the conditions of irreversible gelation. A concentrated sodium silicate solution ([Si]=7 mol/l, pH=11.56, Si/Na=1.71) was used as starting solution. 29Si NMR spectroscopy, SAXS and elementary chemical analyses (ICP-AES) were used to characterize the various solutions. Acidification of initial solution, leads in a range of relatively low pH and [Si] to the formation of various gels: (i) reversible transparent gels stable in time, (ii) soluble white gels leading to the formation of a soluble solid during ripening, (iii) irreversible gels that provide a syneresis leading to the formation of a strongly solid based on a soluble phase similar to white gels and an insoluble silica-type phase. Gelation results from the formation of small particles, which grow in number and size. The mechanism of ripening can be explained by a dissolution / precipitation mechanism.

CK-1:IL08 **Preparation and Stability of Alkali Activated Materials from Slags and Fly-ashes**

Vlastimil Bilek, ZPSV a.s., Brno, Czech Republic

Alkali-activated concretes are relatively well-known composites. They show good mechanical properties, good resistance to the attack of a variety of chemical media and some other suitable properties. For their practical application various problems must be solved - for example the optimum composition of binders (slag + fly ash), content of alkaline activator and its nature (role of cation - Na+ or K+ in activator). These properties are discussed in this paper, which can be divided into these parts: - Time of setting of mixtures from two kind of blast-furnace slags (Czech and Ukrainian) and with replacement of the slag by fly ash and limestone - optimum composition of alkali activator (silicate modulus) will be presented for different mixtures. - Workability and strengths development of mortars from slag and with replacement of slag by some admixtures (fly ash, limestone, stone powder - filler). Workability of mixtures is better with K+ ions in activator and this also enhances strengths. - Efflorescence avoiding by introduction of K+ ions into mixture. - Mechanical properties of self compacting alkali-activated concrete with slag and fly ash. - Freezing and thawing and scaling resistance. It was published that the freezing and thawing resistance of these materials can be excellent. But some other experiments show that the resistance (freezing and thawing resistance index) is strongly affected by the content of alkali activator. Also entrained air can enhance freezing and thawing resistance as in the case of usual concrete. - Long-term development of mechanical properties of AAM is recorded. The development of fracture characteristics and strengths for AAMs composed of slag and slag + fly ash will be presented for up to 2 years old specimens. Some possibilities of making the alkali activated concrete more beneficial for practice are searched on the basis of these aspects.

CK-1:IL09 **Recent Development of Magnesium-based Cements - Magnesium Phosphate Cement and Magnesium Oxychloride Cement**

Zongjin Li*, Fei Qiao, C.K. Chau, Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Hong Kong, China

The recent achievements in research and development on two types of environmental friendly cementitious materials, magnesium oxychloride cement and magnesium phosphate cement, are presented in this paper. For magnesium oxychloride cement, the achievements reported include: new evaluation method of reactivity of raw material, determination of the strength development, water resistance, and identification of phase composition in the cement paste. For magnesium phosphate cement, the formulation, the reaction mechanism, mechanical properties including strength, bond ability to old concrete substrate, volume stability, microstructure and performance as rapid repair material in civil engineering are reported.

CK-1:L10 **Study and Characterization of in-situ Geomaterial Foam by DTA-TGA Coupled with Mass-spectroscopy**

E. Prud'homme*, P. Michaud, S. Rossignol, GEMH, Limoges, France; E. Joussein, GRESE, Limoges, France ; J-M. Clacens, S. Arii-Clacens, LACCO, Poitiers, France

Geopolymers are amorphous three-dimensional alumino-silicate binder materials which may be synthesized at room temperature by alkaline activation of alumino-silicates obtained from industrial wastes, calcined clays, natural minerals or mixtures of two or more of these materials. Previous work has already shown the possibility to obtain geopolymer potassium foam by adding industrial waste to a geopolymer reactant mixture. The foam formation is cause by redox reaction between free silicon and water in basis middle which produce dihydrogen gas. The preparation of geomaterial foams is based on alkali silicate, alkali hydroxide, industrial waste and clays. The mixture was transferred to an open polyethylene mould and placed in an oven at 70 °C for 24 hours. The aim of this work deals with the understanding of the foam formation and with the study of thermal foam behavior throughout mass-spectroscopy coupled with DTA-TGA and in-situ XRD. Study of thermal behavior has revealed the foam carbonation and the apparition of a phase at elevated temperature combined with water outgassing. The formation of foam was investigated with various amounts of silica fume and under various atmospheres in order to compare kinetic of dihydrogen production.

CK-1:L11 **Geopolymer Synthesis from SiO2 and Al(OH)3 Precursors Using K and Na Activators**

Maricela Lizcano, Hyunsoo Kim, Miladin Radovic*, Texas A&M University, College Station, TX, USA

The many impurities found in aluminosilicate sources such as steel slag and fly ash can deter the understanding of complex geopolymer materials. In this study, pure SiO2 and Al (OH)3 precursors are activated using KOH and NaOH alkaline solutions to synthesize geopolymers. The polymerization mechanism is examined as a function of chemical composition (molar ratios), mixing methods and curing environments. Amorphous silicon (IV) oxide was mixed with a Na or K aluminate solution using three different mixing methods and three curing environments. XRD and NMR results indicate geopolymerization in all cases for Si/Al ratios of 2 and 4. An amorphous hump is visible for 2?= 18-30 in XRD for all examined samples. However, in some cases, crystalline peaks that correspond mostly to the unreacted material are also noted in XRD spectra. The 29Si NMR spectra displayed a SiQ4 (1Al) (Si-O-Al) and 27Al NMR spectra indicated a variation of coordination 4 Al and coordination 6 Al ratios, respectively. Effect of composition, mixing and curing conditions on the structure of geopolymers and presence of crystalline phases in the cured materials are discussed in more details in this paper.

CK-1:L12 **Fly Ash Beneficiation and Geopolymer Properties**

N.W. Chen-Tan*, A. Van Riessen, Curtin University, Perth, Western Australia, Australia

Fly ash geopolymer has demonstrated excellent properties as a building material though due to the large variation of fly ash composition from different power stations and poor consistency between feedstock batches, adaption of a generic “recipe” will not be readily achievable. However beneficiation of the fly ash feedstock can improve both the reactivity of the fly ash and the reproducibility of the resultant geopolymer product. A robust characterisation procedure was conducted prior to fly ash beneficiation to determine the base amount of amorphous content. Beneficiation consisted of two steps, the removal of secondary unreactive phases and the increase of surface area of the reactive amorphous content. The modified feedstocks were analysed using a suite of techniques to determine phase composition and relative reactivity. The feedstocks were then used to produce geopolymer and compared with an unmodified feedstock geopolymer. The advantages and drawbacks of fly ash beneficiation for geopolymer production will be presented.

CK-1:IL13 **Geopolymer Binders in Composite Cements and Ceramic-like Materials**

Ch. Kaps*, M. Hohmann, Bauhaus-University Weimar, Building Chemistry, Weimar, Germany

Geopolymers are well-known as alkali activated alumino-silicates with advantageous binder properties. Two main steps prove to be important for a successful generation: 1. Thermal activation of the aluminosilicatic raw materials. 2. Alkali activation of the thermal treated products To reduce the CO2 emission, on the one hand there is an inforced actual trend in the commercial cement production for minimization of OPC contents and for manufacture of puzzolan/composite cements (CEM II and III). With such a destination, we carried out the thermal activation (1.) of clay minerals (550-950°C) under different gas atmospheres (reducing and oxidizing) and studied the solving behaviour (Si/Al ratio). The discussion will be focused on a comparison of the puzzolanic reaction, caused by Ca(OH)2, with the alkali activation of the formed “meta-clays”. On the other hand, there is a general interest for acid-resistant mineral binders. Using an amorphous iron oxide (Fe2O3 . nH2O) we prepared under acidic activation (in contrast to 2.) with H3PO4 network binders. The setting behaviour depends remarkably on the mixture ratio and additives (Fe, KH2PO4). The structure and the strength of these geopolymer-like materials will be discussed, also with respect to cold-setting phosphate ceramics.

CK-1:IL14 **Dissolution-reorientation-polycondensation Processes of Metakaolin in Alkaline Solutions Related to Geopolymerization**

Yunsheng Zhang, Jiangsu Key Laboratory for Construction Materials, Southeast University, Nanjing, P.R.China

Geopolymer is a novel type of inorganic cementitious material, which has become a hot topic across the world. Geopolymerization process of metakaolin in alkaline solutions shows important effects on final properties of hardened geopolymer. In this paper all the possible reaction pathways involved in dissolution-reorientation-polycondensation process of metakaolin in alkaline solution were studied according to the thermodynamic theory. The corresponding reaction energy of every possible pathway was also calculated using the computation chemistry method- semi-empirical AM1 calculation. The optimum reaction pathway was analyzed based on the energy-minimized principle. The calculation results showed that strongly alkaline accelerated the dissolution of 6-membered tetrahedron rings of SiO4 or AlO4 tetrahedron representing the molecular structure of metakaolin during the dissolution process. Si-Al hybrid reorientation should theoretically be the primary reorientation pathway during reorientation process. Framework clusters should be primary polycondensation products during the polycondensation process. These observations were further verified by MAS-NMR. The above studies enhanced understanding of formation mechanisms of metakaolin in alkaline solutions related to geopolymerization.

CK-1:L15 **Use of Sodium Silicate Gel as Precursor of Binder for Cold Consolidated Materials**

M.T. Tognonvi, J. Soro*, S. Rossignol, J.P. Bonnet, GEMH-ENSCI, Limoges, France

Consolidation of cements and geopolymers can be explained by the formation of CSH and/or alkali silicate or alumino-silicate gels. These gels are formed in situ during materials setting in alkaline medium and are difficult to control. In order to understand such system, a study concerning the use of sodium silicate gel as binder was initiated to manufacture consolidated materials with silica, sand and/or zircon. The gels used as precursor of binder were synthesised by acidifying with hydrochloric acid a concentrated sodium silicate (Si/Na = 1.7; pH = 11.56). The consolidated materials were obtained by mixing the previous solution with the granular materials. Samples were dried at 25 °C and setting occurred from three days to one week according to the composition. Reaction mechanisms were followed by FTIR spectroscopy. Microstructures of fresh and dry samples are respectively observed by cryogenic and classic SEM measurements. Mechanical properties of samples were characterized by three point bending tests. All the results show a polycondensation reaction in the fresh mixture. The microstructure and mechanical properties of materials are similar to those of cement materials.

CK-1:L16 **New Geopolymers Based on Rice Husk Ash**

Yolanda Luna Galiano*, Constantino Fernández Pereira, José Ramón Molas Flores, University of Seville, School of Engineering, Chemical and Environmental Engineering Department, Seville, Spain

Rice husk ash (RHA) has been studied as source material in geopolymer systems as an alternative to other agents such as coal combustion fly ash. This silica-rich material was used in different geopolymer mixtures. Kaolinite and metakaolinite were used as alumina source and different aqueous solutions were used as activating alkaline liquor (8M NaOH, 8M KOH, potassium and sodium silicate). The presence of unburned matter in RHA is an important issue and for this reason was one of the variables first studied. Other problems are due to the difficulty to get a good geopolymer mixture. The water amount used, the addition rate and the mixing process seem to be the most important parameters in order to reach a good workability. Compressive strength and degree of reaction tests were measured in order to study the effects of the following variables: Al content in the mix, the use of calcined or non calcined materials and the use of Na or K source solutions. The main conclusion found was that it must be a minimum Al/Si weight ratio to reach a good workability in the mixture. In addition, it was also shown that the effect of silicate activating solutions is more remarkable than sodium or potassium hydroxide solutions, the first showing shorter curing times and higher compressive strength.

CK-1:L17 **Geopolymer Development by Powders of Metakaolin and Wastes in Thailand**

Chayanee Tippayasem[1]*, Sansanee Bunsari[3], Lada Punsukumtana[3], Suvimol Sajjavanich[2], Duangrudee Chaysuwan[1], [1]Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok, Thailand; [2]Department of Civil Engineering, Faculty of Engineering, Kasetsart University, Bangkok, Thailand; [3]Department of Science Service, Ministry of Science and Technology, Bangkok, Thailand

Geopolymer has been developed as an alternative material to Portland cement. Geopolymer is based on the polymerization of alkaline activation and oxide of silicon and aluminium. These oxides can be found in many pozzolanic materials such as metakaolin and the wastes from agricultures and industries, e.g., fly ash, bottom ash, bagasse ash and rice husk ash. Pozzolanic materials were used as source materials for making geopolymers into 5 different types. Sodium hydroxide concentration of 10M (10MNaOH) and sodium silicate (Na2SiO3) solutions were used as alkaline activators by the mass ratio of Na2SiO3/NaOH at 1.5. The mixtures were cast in 50 × 50 × 50 mm. cubes. After casting, the geopolymers were cured at 80 °C for 24 hour in oven and at room temperature for 7 days. The pozzolanic materials effects, the liquid alkaline/solid ratio and the ash/metakaolin ratio were studied and characterized. X-ray fluorescence (XRF) was used to determine the percentages of silica and alumina in order to verify the proper ratio of the ash/metakaolin. The study also included the impact on physical properties such as compressive strength, density and water absorption. The samples were analyzed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques.

CK-1:IL19 **Chemical and Physical Features Governing the Properties of Geopolymers Produced from Fly Ash**

H.W. Nugteren*, M.T. Kreutzer, Delft University of Technology, Product and Process Engineering Group, Delft, The Netherlands; G.-J. Witkamp, Delft University of Technology, Process Equipment Group, Delft, The Netherlands

Tests with 18 different coal fly ashes (optimised mix compositions: ash/slag/activator/water), showed a range of compressive strengths (up to 100 MPa) and paste behaviours. Three interrelated factors have influence on these results. 1) reactivity of fly ash determines the rate of dissolution of ash particles. 2) chemical composition of glass determines the chemical composition and properties of the geopolymer formed. 3) ratio geopolymer matrix / particles to be cemented, determines strength of final product. Reactivity of ash depends on glass content and glass chemistry. Ash dissolution tests in alkaline environment show that glass with a high content of network disturbers dissolves easier and faster. Free lime reduces setting time and decreases compressive strength. K-silicate activator resulted in highest strengths. Fine size and high sphericity particles favour dense packing and high strength. Particle size and specific surface influence liberation of reacting components from ash. Separated fractions did not show a clear relation because of differences in chemistry, but by grinding higher strengths resulted for finer fractions, although workability and setting time reduced. With a Na-aluminate waste effluent activator, an all-residue geopolymer (60 MPa) could be produced.

CK-1:L20 **Physical, Mechanical and Micro-structural Properties of Fly-Ash Based Geopolymeric Bricks Produced by Pressure Forming Process**

Omer Arioz[1], Kadir Kilinc[2]*, Mustafa Tuncan[2], Ahmet Tuncan[2], Onur Zeybek[2], Taner Kavas[3], [1]Cimsa, Ready-Mixed Concrete Company, Eskisehir, Turkey; [2]Department of Civil Engineering, Faculty of Engineering & Architecture, Anadolu University, Eskisehir, Turkey; [3]Department of Materials Science & Engineering, Faculty of Engineering, Afyon Kocatepe University, Afyonkarahisar, Turkey

Geopolymer is a new class of three-dimensionally networked amorphous to semi-crystalline alumino-silicate materials, and first developed by Professor Joseph Davidovits in 1978. Geopolymers can be synthesized by mixing alumino-silicate reactive materials such as kaolin, metakaolin or pozzolans in strong alkaline solutions such as NaOH and KOH and then cured at room temperature. Heat treatment applied at higher temperatures may give better results. Depending on the mixture, the optimum temperature and duration vary 40-100 °C and 2-72 hours, respectively. The properties of geopolymeric paste depend on type of source material (fly ash, metakaolin, kaolin), type of activator (sodium silicate-sodium hydroxide, sodium silicate-potassium hydroxide), amount of activator, heat treatment temperature, and heat treatment duration. In this experimental investigation, geopolymeric bricks were produced by using F and C-type fly ash, sodium silicate, and sodium hydroxide solution. The bricks were treated at various temperatures for different hours. The compressive strength, density and water absorption of F-type fly ash based geopolymeric bricks were determined at the ages of 7, 28 and 90 days. The compressive strength, density and water absorption of C-type fly ash based geopolymeric bricks were determined at the age of 7 day. Test results have revealed that the compressive strength values of F-type fly ash based geobricks ranged between 5 and 60 MPa. However, the compressive strengths of C-type fly ash based geobricks varied between 8 and 13 MPa. It has been found that the effect of heat treatment temperature and heat treatment duration on the density of F-type and C-type fly ash based geobricks was not significant. The water absorption values values of F-type fly ash based geobricks ranged between 10 and 25%. However, the water absorptions of C-type fly ash based geobricks varied between 25 and 35%. It should be noted that the spherical particle size increased as the heat treatment temperature increased in the microstructure of F-type fly ash based geobricks treated in oven at the temperature of 60 °C for 24 hours.

CK-1:L21 **Lightweight Geopolymer Materials for Insulating Applications: Electric and Thermal Properties**

E. Kamseu[1]*, C. Leonelli[1], A. Libbra[2], A. Muscio[2], [1]Department of Materials and Environmental Engineering, University of Modena and Reggio Emilia, Modena, Italy; [1]Department of Mechanical and Civil Engineering, University of Modena and Reggio Emilia, Modena, Italy

The thermo-chemical transformation (at 700 °C) of kaolinite to metakaolinite conducts essentially to an amorphous matrix with relative low density. By reacting this amorphous phase with alkali silicate binder previously activated with high concentrated alkali-hydroxyde solution (~7.5M), we obtained a structural matrix being nano to micro phases interlocked in an amorphous system together with nano to micro pores. Five compositions with Si/Al molar ratios from 1.23 to 2.42 were developed reducing the thickness of the materials while preserving the mechanical properties. The cracks and fracture behaviour of the final products were assessed under chemico-environmental and mechanical stresses and were correlated to the elastic properties to evaluated the toughness of these compositions. Thermal dilatation and thermal conductivity as well as electrical properties were evaluated and compared to the standard insulating materials of the aluminosilicate group. Controlled artificial nano and micro pores were then added progressively to the matrices that enabled to reduce the density to <1 g/cm3 maintaining under control the resistance to cracks and fracture behaviour. High Si/Al ratios conducted to homogeneously distributed pores mainly in nano and micro sizes with 60% of total porosity compared to low Si/Al ratios (65-70%). The thermal conductivity decreases from 0.24 + 0.005 to 0.14 + 0.005 W/(m.K) and the specific electrical resistance was 0.6 x 1010 Ω m. The matrix the porosity and density as well as the thermal conductivity of the products obtained permitted to described lightweight geopolymer as potential insulating materials for Engineering applications. It was possible to design fine size pores and homogeneous matrix by considering the starting Si/Al ratio.

CK-1:L22 **Durability of Geopolymer Concrete upon Seawater Exposure**

S. Astutiningsih*, D.M. Nurjaya, H.W. Ashadi, D. Dhaneswara, N. Swastika, Faculty of Engineering, University of Indonesia, Kampus UI, Depok, Indonesia

Indonesia, an archipelagic country with 17,504 islands stretching along the equator, has the second longest coastal line in the world, i.e. 8100 km. Marine infrastructure which requires special precaution is thus important in the country with 5.8 million km2 of marine area. The presence of aggressive Cl ions in seawater decrease the durability of conventional Portland cement concrete which is the dominant material used for construction. On the other hand, geopolymer cement is claimed to be more resistant to chemical attack than Portland cement due to the absence of hydrated calcium - silicate compounds or CSH. This study on geopolymer concrete for marine application is in progress. Geopolymer concrete with designed strength of 40 MPa has been mixed from coarse aggregates, sands and geopolymer pastes. Two kinds of pastes are synthesized from different precursors, i.e. class C fly ash and dehydroxylated kaolin, using sodium silicate solution as the activator. Compression test pieces of 15x15x15 cm3 of both geopolymer and Portland cement concretes (ASTM C39) will be cast and cured. Geopolymer concretes will be cured at room temperature for 1 day while Portland cement concretes will be immersed in water for 28 days to provide complete hydration. After complete curing, these samples will be immersed in ASTM seawater (ASTM D1141-90) for 30-days, 60-days and 90-days. Compressive strength of both kinds of concretes after immersion will be compared with the as-cured samples. Microstructure characterization of the seawater-exposed samples will be performed using SEM and identification of new phase(s) / compound(s) produced after immersion will be done using powder x-ray diffraction. Water-soluble compounds that might be produced after immersion will be quantified by leaching the samples in water and analyze the dissolved ions using atomic absorption spectroscopy.

Session CK-2
Characterization

CK-2:IL01 **The Application of Micromechanics on Alkali-activated Materials**

F. Skvara, Institute of Chemical Technology Prague, Prague; V. Smilauer*, J. Nemecek, L. Kopecky, Czech Technical University in Prague, Faculty of Civil Engineering, Department of Mechanics, Prague, Czech Republic

Chemistry plays an important role in characterization and understanding of alkali activated materials. In addition, micromechanics offers several methods complementing the research of such multidisciplinary and multiscale materials. Our micromechanical analysis starts at the submicrometer scale of the geopolymer binder revealing intrinsic elasticity of phases characterized by nanoindentation technique. The combination with a model of alkali activation upscales the elasticity further to the scale of binder and concrete thus validating used models. Strength-porosity relationship is completely different with regard to portland-based systems. Fracture micromechanics offers a feasible explanation and leads to a consistent alkali-activation model on the submicrometer scale.

CK-2:IL02 **The Alkali-activation of Aluminosilicates - Some Chemical Perspectives**

Donald E Macphee, Ines Garcia Lodeiro*, University of Aberdeen, Old Aberdeen, Scotland

Despite our dependency on concrete for the built infrastructure, the cement industry faces growing environmental pressures on its CO2 emissions. The cement community response has included increased research towards alternative environmentally sustainable binders. What exactly are these and what makes them different from conventional Portland cement? This presentation takes a look at some of the chemical drivers underlying the cement reaction, placing these in the context of conventional (familiar) cement systems, and extends these ideas to other systems, including alkali-activated binders, which may partially replace Portland cement in constructional concretes. On this basis, the chemical behaviour of binder systems which define microstructure development, and hence strength and durability characteristics, is reviewed, offering possibilities for optimisation of materials selection and activation conditions.

CK-2:L03 **Mechanical Properties of Metakaolin Geopolymers: A Microstructural Study**

Elie Kamseu, Cristina Leonelli*, DIMA, Università di Modena e Reggio Emilia, Modena, Italy; Antonella Tucci, Leonardo Esposito, Centro Ceramico Bologna, Bologna, Italy

Metakaolin geopolymers bonded with potassium silicate were prepared with different raw materials characterized by Si/Al molar ratio between 1.15 and 2.19 commonly used for structural applications. Sample preparation was carefully optimized for the mechanical testing machinery so that to achieve a reliable process. Shaping in plastic moulds and curing for 24 hrs in a plastic bag were enough to allow specimens to dry and consolidate at room temperature. In order to determine the consolidating process, the materials were subjected to compression tests as well as to 3-point and biaxial bending tests. The mechanical behaviour after the exposure to the environment was also determined.

Extensive observations of the fracture surface by SEM-Scanning Electron Microscope and fractografic analysis by using OM-Optical Microscope were performed both to identify the fracture origin and to investigate the microstructure of these materials, in particular the conditions of fracture propagation and the dependence of mechanical strength on the porosity. These observations, correlated with the results of the mechanical characterisation, allowed to attribute to the porosity distribution a critical role for the behaviour of geopolymers as structural materials.

CK-2:L04 **High-temperature Mechanical Property of Cf/geopolymer Composites After Heat Treatment and Repeated Impregnation by Sol-SiO2**

Dechang Jia*, Peigang He, Tiesong Lin, Meirong Wang, Harbin Institute of Technology, Harbin, P.R. China

Unidirectional carbon fiber reinforced geopolymer composite was prepared by ultrasonic-assisted slurry infiltration method and then heat treated at 1100 °C to enhance its mechanical properties. The as-heat treated composite was then impregnated with Sol-SiO2. The ambient and high temperature mechanical properties of composite were investigated. Sol-SiO2 can successfully seal the cracks and pores formed during heat treatment. After 4 impregnation cycles using 30wt% Sol-SiO2, most cracks and pores could be sealed and composite gets to a relative density of 93.6% and showed a dense microstructure. Ambient strength of composite after impregnation was enhanced by 20% relative to its original state before impregnation. The impregnated composite showed favorable high temperature mechanical strength, and retained 88.5%, 80% and 78% of its ambient strength at 700, 900 and 1100 °C, respectively. All composites fractured in a non-brittle manner at ambient and high temperature.

CK-2:L05 **Evaluation of the Stability of Waste-based Geopolymeric Artificial Aggregates for Wastewater Treatment Processes Under Different Curing Conditions**

I. Silva[1]*, J Castro-Gomes[2], A. Albuquerque[2], [1]Castelo Branco Polytechnic Institute and Centre of Materials and Building Technologies, University of Beira Interior, Covilhã, Portugal; [2]Centre of Materials and Building Technologies, University of Beira Interior, Covilhã, Portugal

Waste geopolymeric artificial aggregates (WGA) with different atomic ratios of mining waste mud/Na$_2$SiO (4 to 5) and Na$_2$SiO/NaOH (1.25 to 5) were produced (112 samples) using curing temperatures between 20 °C and 130 °C and its structural stability and pH variation after immersion in water was observed during 3 months. Results showed that samples cured at 20 °C for a minimal of 35 days presented good stability in water and pH decreased from 10 to 7 in 12 days. Additional samples of a WGA with waste mud/Na$_2$SiO of 4 and Na$_2$SiO/NaOH of 5 (352 samples) cured at 20 °C and 80 °C were produced and compressive strength was determined in dry conditions, for 13 curing ages and 15 water immersion periods (up to 14 weeks). Results showed that increasing temperature to 80 °C accelerated compressive strength gain but only during the first 3 weeks (up to 15.4 MPa). After 24 hours of immersion in water compressive strength decreased to half of the initial values (determined in dry conditions) in all samples and, therefore, the increase of temperature did not bring benefits to WGA strength in water. Regardless the curing temperature and the dry curing age comprehensive strength stabilizes between 1 MPa and 2 MPa after 4 weeks immersion in water, which are values that makes WGA suitable to be used as bed material for wastewater treatment processes.

CK-2:IL06 **Atomic Structure and Microstructure of Geopolymer and Crystallized Geopolymer Ceramics**

W.M. Kriven,* J.L. Bell, P.E. Driemeyer, P. Sarin, R.P. Haggerty, N. Xie, University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering, Urbana, IL, USA

The formation of pollucite (CsAlSi2O6) and leucite (KAlSi2O6) from geopolymer precursors was studied using dilatometry, thermogravimetric analysis (TGA), differential scanning calorimetery (DSC), high temperature in-situ synchrotron X-ray diffraction (HTXRD and pair distribution function (PDF) analysis), as well as a variety of microstructural characterization techniques (MIP, BET, SEM, EDS, TEM, SAD, HREM, STEM). It was found that crystallization temperatures and activation energies are lower using geopolymer gels compared with most other ceramic preparation techniques. Both phases were found to crystallize at around 900-950°C, and the resultant ceramic phase consisted of a crystalline phase surrounded by an amorphous matrix. Leucite composition geopolymers crystallized up to 80 wt% KAlSi2O6, which is higher than one can obtain via traditional dental porcelain routes. The microstructures of porous geopolymer bodies were converted to ceramics and examined by a variety of microstructural characterization techniques. Leucite glass-ceramics were fabricated by cold isostatically pressing K2O.Al2O3.4SiO2.11H2O geopolymer powders into pellets followed by firing at 950-1200 °C (every 50 °C) in air. Leucite formation was observed in specimens heat treated to ≥1,000 °C.

CK-2:IL07 **In Situ Characterization of Fresh and Aged Geopolymer Materials**

S. Rossignol, GEMH ENSCI, Limoges, France

Geopolymers are amorphous three-dimensional alumino-silicate binder materials. They are synthesized at room or slightly elevated temperature by alkaline activation of alumino-silicates obtained from industrial wastes, calcined clays, natural minerals or mixtures of two or more of these materials. Highly porous ceramics can be prepared (i) by impregnation of organic foam with mineral materials foams can be synthesized, (ii) using a pore forming agent or (iii) by incomplete firing of green body. In previous work, a geomaterial foam was obtained from alkaline silicate and alkaline hydroxide solutions with the addition of clays and silica fume. The aim of this paper is to examine the foam formation in various conditions, to define the role of the solid phase structure depending on Al2O3 and SiO2 and notably the clay nature. The understanding of the foam formation is investigated ventilated oven through mass-spectroscopy coupled with DTA-TGA measurements (in various atmospheres) and by ATR spectroscopy. The influence of the used raw materials is evaluated by structural data determined by ATR spectroscopy, in situ XRD and cryo-SEM measurements.

CK-2:L09 **Comparative Study of the Consolidation Process and Properties of Clay Based Geomaterials and “Geomimetic” Lateritic Clay Based Materials**

G.L. Lecomte*, G. Lecomte, Groupe d’Etude des Matériaux Hétérogènes, ENSCI, Limoges, France; A. Wattiaux, Institut de Chimie de la Matière Condensée de Bordeaux, Pessac, France

The present work focus on the elaboration of low energy consuming materials and the correlation between their final properties and the fabrication route. For this purpose, geomaterials have been elaborate using a common raw clay material. Also an original route has been developed to elaborate “geomimetic” materials. The raw material consists of lateritic clay, whereas the main reactives are namely: nitric acid, fulvic acid, and calcium hydroxide in an aqueous medium. In both ceramic materials, the strengthening process and the final characteristics of the as obtained products have been investigated. Namely: the characteristic compressive strength and the resistance to water seeping and wearing. The geomaterials exhibits a good resistance towards water seeping and wearing, but the products obtained using Portland cement present a greater characteristic compressive strength than with lime. “Geomimetic” materials are also water resistant. In fact, the products elaborated using nitric acid exhibit the best characteristic compressive strength, namely 20 MPa. While with fulvic acid, an environmental friendly organic acid, a characteristic compressive strength of 12 MPa is obtained. Thus the latter appears competitive towards usual stabilized earth and concrete building materials.

CK-2:L11 **Development of a National Database for Facilitating Widespread Recycling of Fly Ash into Geopolymer Concrete**

Erez N. Allouche*, Ivan Diaz, Dept. of Civil Engineering, Louisiana Tech University, Ruston, LA, USA

The variability of fly ash as source material for geopolymer was investigated and statistically assessed. The results of elemental chemical analyses, X-ray diffraction (XRD) and particle size distribution (PSD) of thirty (30) fly ash samples are presented and used as variables for the assessment. Geopolymer paste and concrete specimens were prepared for each fly ash sample. Paste specimens were subjected to XRD while concrete specimens were evaluated for setting time (“pot life”), compressive and flexural strengths, elastic modulus and Poisson’s ratio. A statistical assessment was undertaken to analyze the correlation between the chemical analysis, XRD and PSD of the fly ash precursor and the properties of the fresh geopolymer mix as well as the mechanical characteristics of the resulting geopolymer concrete. Based on the statistical analysis optimal ranges of chemical elements, amorphous content and fineness inherent to the fly ash were identified for fly ash that are expected to be suitable stockpiles for pre-cast and cast-in-place applications.

CK-2:L12 **New Geopolymers Based on Electric Arc Furnace Slag**

M.C. Bignozzi*, F. Sandrolini, Dipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna, Bologna, Italy; L. Barbieri, I. Lancellotti, Dipartimento di Ingegneria dei Materiali e dell’Ambiente, Università di Modena e Reggio Emilia, Modena, Italy

Geopolymer systems have a structure, mainly amorphous, obtained by alkali-activated polymerization of alumino-silicate sources. Although the most part of studies has been addressed on metakaolin (MK) based geopolymers with the aim to understand the reaction mechanism and operative conditions, geopolymers based on industrial waste have recently been developed. In fact, several types of industrial waste are rich in silica and alumina thus fulfilling the first requirement necessary for geopolymerization. Investigations on carbon fly ash and blast furnace slag as unconventional sources of alumino-silicate are currently running, highlighting that the geopolymerization process can successfully occur. Indeed, the possibility to find other industrial waste to be recycled as geopolymer materials is a challenging issue. Accordingly, the geopolymerization of electric arc furnace slag (EAF-S) is reported. Arc electric furnace technology is widely used for steel production as it has a less severe impact on the environment than that one based on blast furnace. Geopolymers based on 100% EAF-S and on MK and EAF-S in different amounts have been prepared and characterized. The results are discussed and compared with those obtained for geopolymers made of 100% MK.

CK-2:L13 **Phase and Strength Evolution of Fly Ash Geopolymers Exposed to Standard Fire Conditions**

W.D.A. Rickard*, A. van Riessen, J. Temuujin, R.P. Williams, Centre for Materials Research, Curtin University of Technology, Perth, WA, Australia

Geopolymers are a synthetic inorganic polymer produced by the alkali activation of aluminosilicate raw materials. Geopolymers have traditionally been intended as a replacement concrete but more recently have been applied to high temperature applications due to their intrinsic thermal resistance. This project investigated the prospect of adapting geopolymers for use as a fire proofing material with the intended application as a fire resistant coating. The phase and strength evolution of geopolymers exposed to a standard fire heating curve was investigated. Geopolymers were synthesised from three Australian fly ashes of varying composition. It was observed that fly ashes with a high iron content (>10wt%) experienced an increase in crystalline iron phases after exposure and a subsequent loss of mechanical strength, believed to be due to the volumetric changes caused by the growth of the iron phases. Other phase changes, such as the growth of feldspars, were observed in all samples. The strength of samples with a low iron content (<5wt%) was observed to increase after exposure. Test results from low iron fly ash geopolymers suggest they may be suitable for use as a fireproofing material due to their high strength retention and favourable phase changes at high temperatures.

CK-2:L14 **Evaluation of the Thermal Conductivity of Model Materials and Elaboration of a Porous Material**

J.Bourret*, E. Prud'homme, S. Rossignol, D.S. Smith, GEMH, ENSCI, Limoges, France

The development of highly performant thermal insulators is a major issue in the field of high temperature processing and equipment as well as in the building sector. Furthermore, thermally insulating materials based on fibres or fine particles are being progressively phased out. Alternative materials with a very low thermal conductivity which combine energy saving and environmental protection are the topic of modern research. Porous materials have thus been prepared from a solution containing potassium silicate and sodium hydroxide with the addition of kaolin and fumed silica. This method yields a consolidated goematerial foam without requiring thermal treatment above 70 °C. The influence of different parameters on the volume fraction and size of pores, such as drying temperature and chemical composition, were studied. In particular the viscosity of the mixture and the choice of raw materials were found to play an important role. The accuracy of thermal conductivity measurements was evaluated by comparing the steady state heat flow method with the laser flash technique. Careful preparation of samples was necessary. A value of 0.12 ± 0.01 W/m/K was obtained for consolidated foams based on kaolin which contain approximately 70% of porosity.

Session CK-3
Industrialization & Application

CK-3:IL01 **Medium to Long Term Engineering Properties and Performance of High-strength Geopolymer Concrete Systems**

K. Sagoe-Crentsil, CSIRO Materials Science and Engineering, Highett, Victoria, Australia

The medium to long term engineering performance of high-strength Geopolymer concrete systems are largely dependent on fluid ingress and the transport phenomena that govern permeability of structural members exposed to aggressive environments. For the purpose of analysing durability performance, both high pressure water and gas permeability testing of fly-ash based geopolymer concretes have been assessed for samples cured under ambient and steam exposure conditions at 65 °C. The observed mean permeability coefficient values for gas(k) and water(Kw) of structural grade concrete was respectively 1.36E-16m2 at 300kPa gas pressure and 1.70E-10m/s at 525kPa water pressure. While mean gas permeability values were comparable to reference OPC systems the corresponding water permeability coefficient data for geopolymer systems were typically three-fold higher. The transport properties of OPC concrete systems are typically governed by water-to-cement ratio and the degree of hydration which is linked to the level of porosity and its interconnectivity. However, corresponding permeability of Geopolymer concrete appears to be dictated by an inherent mesoporous capillary pore network structure for which transport properties are less sensitive to system mix design and cure conditions. The Paper examines global implications of increased permeability on key durability parameters such as chloride diffusion, carbonation rates and steel reinforcement corrosion on long-term engineering and durability performance.

CK-3:IL02 **Geopolymers in Conservation of Stone Monuments and Buildings**

Amandio Teixeira-Pinto, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal

As a major construction material during centuries, stone is present in important monuments and buildings, which being part of our Culture belong to a common History that has to be preserved and transmitted to the future. This is the main reason to build up efficient methods of repairing damages caused by Nature's erosion, the action of Man or the elapsing of Time. The degradation of the stone is sometimes so advanced that there is no support for stabilization procedures. And if reversibility is in practice impossible, a great part of recovering solutions may involve the definitive removal and substitution of important parts of the stone monument itself. Several authors favour this drastic solution as the only procedure of preserving indefinitely an architectonic patrimony which it is pretended to be unchangeable. The alkaline activation of aluminosilicates (geopolymers) or calcium rich minerals opens the way for the in-situ repairing stones, then avoiding the need for removal. The alkaline activation is, in a certain way, the reversal process of evolution of what is generally known as the degradative phenomena that explains the major alterations of feldspatic or micaceous mineral constituents in great number of rocks. Some real tests are presented. Final results, verified after 6 years under normal outside conditions, have shown that the agglomerated rock is stable and does not differ substantially from the natural one.

CK-3:L03 **Use of Local Raw Materials for Construction Purposes**

H. Rahier*, M. Esaifan, J. Wastiels, Vrije Universiteit Brussel, Brussels, Belgium; I. Aldabsheh, F. Slatyi, M. Alshaaer, H. Khoury, Materials Research Laboratory, University of Jordan, Amman, Jordan

Since some years research is going on in Jordan to produce construction materials, starting from local raw materials. Geopolymers have the benefit that they have a smaller environmental impact than concrete, but also the main raw material, for instance kaolinite, is often locally available. To minimize the production cost, the kaolinite will be used as such and thus not be dehydroxylated. The aim of this research is to: -find out which local raw materials can be used (reactive and filler); -optimize the production (composition, curing) of bricks, tiles; -find out how to do the production in the field; -make a water reservoir for water harvesting. The proposed raw materials are kaoline, bentonite, tripoli, porcelanite, diatomite, silica sand, granite, zeolitic tuff, scoria (tuff) and basalt. The reactivity of these materials was tested. With kaolinite specimens with compressive strength of 41 MPa under dry conditions and 23 MPa under immersed water conditions were obtained. Since the materials will be used for the construction of water ponds, the durability of these specimens was tested. Also these materials exhibit good mechanical performance upon heating to 600 °C, opening a possibility for use under elevated temperatures.

CK-3:L05 **Development of Building Materials Through Alkaline Activation of Construction and Demolition Waste (CDW)**

Joana Gonçalves Rapazote*, Cristóvão Laginhas, Amândio Teixeira-Pinto, Universidade de Trás-os-Montes e Alto Douro, Departamento de Engenharias, Vila Real, Portugal

Construction and demolition waste (CDW) is a by-product of construction and demolition activity. It consists mostly of inert and non-biodegradable material such as concrete, plaster, metal, wood, plastics etc. CDW is priority waste in the E.U. due to the increased quantities and volumes that are produced. While retrievable items such as brick, wood and metal wires etc are recycled, the concrete, masonry and tile and ceramic waste, accounting for more than 60% of CDW, are not being currently recycled. The main objective of the proposed study is to develop a process for obtaining newer building materials from CDW using low temperature geopolymerisation in alkaline environment. The two major fraction of the CDW which are not currently being recycled is concrete and cement, masonary and rubbles, and ceramic tile, mosaic and slabs. The major constituent of the first fraction are SiO_2 and CaO along with minor concentration of Al_2O_3 and Fe_2O_3 and mostly crystalline. The major constituent of the latter are SiO_2 and Al_2O_3 and comprises of crystalline as well as glassy constituents. The aluminosilicate fraction of both fractions will actively participate in the reaction and for the ASH gel (A= Al2O3, S = SiO2, H = H2O), which is the main binding phase. Any deficiency in chemical constituents will be compensated by addition of suitable material, e.g., AL2O3 can be compensated with a source of alumina which will be added for alkaline activation reaction. The remaining non alumino-silicate portions such as iron oxide etc will act as filler material. The final product will be a very hard ceramic like product with no leaching of toxic metals. These products can be used for civil engineering applications such as pavement blocks, precast concrete blocks, etc.

CK-3:L08 Geopolymers as Waste Encapsulation Materials: Impact of Anions on the Materials Properties

F. Frizon*, D. Lambertin, Atomic Energy Commission, DEN, Marcoule, Waste Treatment and Conditioning Research Department, Bagnols-sur-Cèze, France

One of the most promising applications of geopolymers is their use as waste encapsulating matrix. These binders are indeed compatible with aqueous waste streams and capable of activating several chemical and physical immobilization mechanisms for a wide range of inorganic waste species. Several works have investigated the immobilization of cations, mainly heavy metals or radioactive wastes, but very few studies are taking counterions, namely anions, into account. The aim of this work is to experimentally investigate the impact of anions with different valences on the materials' properties in regard to the requirements of an industrial process at ambientor slightly elevated temperature: among others setting time, maximum achievable compressive strength or resistance to leaching. The modifications caused by the introduction of monovalent and divalent anions, such as sulphate and nitrate, are also monitored in term of mineralogy, porosity and microstructure. Their immobilization seems to be related to the advancement of geopolymerization reaction. On another hand, depending on the alkali ions used in the activation solution, the anionic species considered may also enhance the precipitation of some zeolithes.

CK-3:L09 Bond Strength of Geopolymers Concrete with Reinforcing Steel

P.K. Sarker*, R. Vasile. Department of Civil Engineering, Curtin University of Technology Perth, Western Australia

Geopolymer is an inorganic alumino-silicate product that shows good bonding properties. Geopolymer binders are used together with aggregates to produce geopolymer concrete which is an ideal building material for infrastructures. A by-product material such as fly ash is mixed together with alkalies to produce geopolymer. Previous research on geopolymer concrete has shown promising potentiality of the material. Structural performance of reinforced concrete depends on the bond between concrete and the reinforcement. Design provisions of reinforced concrete as a composite material are based on the bond strength between the two materials. Since geopolymer binder is chemically different from ordinary Portland cement (OPC) binder, it is necessary to understand the bond strength between geopolymer concrete and steel reinforcement for the material to be used in the construction industry. Pull out test is a method that is commonly used to evaluate the bond strength between concrete and reinforcing bars. This paper describes the results of the pull out tests carried out to investigate the bond strength between fly ash based geopolymer concrete and steel reinforcing bars. Beam end specimens in accordance with the ASTM Standard A944 were used for the tests. In the experimental program, 24 geopolymer concrete and 24 OPC concrete specimens were tested for pull out. The concrete compressive strength varied from 25 to 40 MPa. The other test parameter was the ratio of concrete cover to bar diameter, which varied from 1.71 to 3.62. The reinforcing bars were 500 MPa steel deformed bars. It was found from the test results that the failure occurred by splitting of concrete in the region bonded with the steel bar, in both the geopolymer and OPC concrete specimens. It is also found from statistical analysis of the results that there is no significant difference between the bond strengths of OPC concrete and geopolymer concrete with reinforcing steel bars.

CK-3:L10 Metal Ion Exchanged Geopolymers and Their Applications

O. Bortnovsky[1], P. Bezucha[1], P. Sazama[2], Z. Sobalik[2], Z. Tvaruzkova[2], J. Dedecek[2]*; [1]Research Institute of Inorganic Chemistry, Usti nad Labem, Czech Republic; [2]J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Geopolymers are generally roentgen-amorphous materials; however recent research has proved that they contain nanometer particles probably with zeolitic structure. It has been also confirmed in our investigation that sodium in metakaolin-based geopolymer is easily exchangeable with other cations such as ammonium, cobalt, copper etc. Moreover, according to UV-VIS spectra of Co-geopolymer it has been proved that the local arrangement of Co2+ extraframework ions in cationic positions corresponds to those in high-silica zeolites, such as mordenite, ZSM-5 or beta. Also even potassium and sodium in metakaolin-slag-based geopolymers were successfully exchanged with various ions of transition metals. Therefore it can be truly expected that these metal-exchanging geopolymers would show alike properties and thus potential applications as zeolites, while keeping the advantages of geopolymers, such as simple synthesis procedure, molding into complicated shapes or forming thin highly adhesive layers. These novel applications of metal geopolymers will be presented and discussed.

CK-3:L11 Geopolymer Coating for Rehabilitation of Concrete-Based Wastewater Collection Systems

Erez Allouche, Carlos Montes*, Department of Civil Engineering, Louisiana Tech University, Ruston, LA, USA

Concrete pipes serve as the backbone of the sewer collection system in many North American cities. A large percentage of these pipes are in various stages of deterioration due to microbiological induced corrosion and/or mechanical loading. A common rehabilitation technique for such structures includes the utilization of a cementitious-based coating. However, the durability of these products in harsh environments limits their useful design life. This paper describes the development and full-scale testing of a novel geopolymer mix for spray coating of sewer pipes and manhole structures. The paper presents test results covering the mechanical strength, corrosion resistance and abrasion resistance of the geopolymer grout formulation. Extensive rheology and surface tension studies were performed to ensure that the geopolymer paste exhibits the desirable field characteristics (i.e., adequate pot life, adhesion, sprayability) . The results suggest that the rheology of the geopolymer paste is highly dependent on the chemical composition of the activator solution. A pilot project involving the rehabilitation of a manhole structure in the City of Ruston, Louisiana, is also presented.

CK-3:L12 Recycling of MSWI Residues by Means of Stabilization/Solidification in Geopolymer-based Matrix

R. Cioffi*, F. Colangelo, University Parthenope, Naples, Italy; F. Montagnaro, L. Santoro, University Federico II, Naples, Italy

The applications of geopolymer-based materials range within the fields of new ceramics, cements, matrices for hazardous waste stabilization, fire-resistant materials, asbestos-free materials and high-tech materials. In this work, municipal solid waste incinerator (MSWI) bottom ashes have been used for the synthesis of geopolymeric matrices able to stabilize hazardous fly ashes coming from the same processes. The different MSWI ashes samples have been used not only as received, but also after washing to reduce the chloride content of fly ash and the swelling due to the presence of bottom ash. The products obtained in the different experimental conditions have been characterized from the chemical, environmental and technological points of view. Specifically, infrared spectroscopy (FT-IR) analyses, leaching tests and physico-mechanical characterizations have been made on stabilized/solidified products, respectively.

CK-3:L13 Recycling of Industrial Waste Water by its Immobilization in Geopolymer Cement

D. Tavor*, A. Wolfson, T. Meyohas, S. Ronen, Center of Green Processes, Chemical Engineering Department, Sami Shamoon College of Engineering, Beer-Sheva, Israel

As part of the growing awareness to environmental issues, industrial waste water has become one of the main concerns of the chemical, petrochemical and process industries. Currently, various biological and chemical methods are employed in order to treat industrial waste water.

Yet they have limited ability to decrease organic compounds to the required level, and they are usually compound specific. Geopolymer are amorphous three-dimensional alumino-silicate binder materials. The sources of silica and alumina are pozzolanic materials such as fly-ash, metakaolin and silica fumes. The unique properties of these materials enabled their fast development as alternative environmentally friendly materials. Recently, we studied the recycling of industrial waste water with residual organic compounds by its solidification in geopolymer matrix as a generic method to treat many industrial waste streams, with various organic compounds. In this work, waste water from Teva Pharmaceutical Industries Ltd. which comprises several organic compounds, was soldificated in geopolymer matrix and the leaching of the organic compounds from the matrix was examined. It was found that the leaching was negligible, about 0.2%wt, and comparable to the amount that leached for geopolymer matrix without waste water.

CK-3:L14 How to Assess the Environmental Sustainability of Geopolymers? A Live Cycle Perspective

M. Weil[1]*, K. Dombrowski[2], A. Buchwald[3], [1]Karlsruher Institut for Technologie (KIT), Institute for Technology Assessment and Systems Analysis (ITAS); Germany; [2]Freiberg University of Mining and Technology, Institute for Ceramic, Glass, and Construction Materials, Germany; [3]Bauhaus-University Weimar, Building Chemistry, Germany

Geopolymers as an alternative binder system becoming growing attention in research and development. Outstanding technical properties like high strength, high acid resistance, or high temperature resistance can be unerringly achieved. Thus geopolymers are not only suitable for the development of building products, but is also an interesting binder system for ceramic applications. Besides the technical performance of geopolymers is well investigated, only limited scientific knowledge exists about the environmental impact of geopolymer production. Due to the wide range of suitable raw materials, composition of alkaline activator as well as geopolymer composition a generally statement about the environmental implications cannot addressed to geopolymers. A more detailed analysis and assessment is needed, to provide more diversified statements. The presented contribution will highlight the dominate drivers for the ecological impacts of geopolymers, to provide guidance for the development of geopolymer composition for different applications.

Poster Presentations

CK:P01 Formation of Tetra-coordinated Aluminum in the Low Temperature Ashes

P. Straka, Institute of Rock Structure and Mechanics ASCR, v.v.i., Prague, Czech Republic

Formation of tetra-coordinated Al ([4]Al) in low temperature coal ashes was investigated. Coal samples were air-oxidized at 350 °C for 75 hours and 27Al MAS NMR spectra of obtained ashes evaluated. It was found that chemical shifts at 4 and 72 ppm correspond with those for Al-tetrahydroxo-diphenoxide complex and [4]Al, resp. So, in the presence of coal organics the [4]Al can be formed under low temperature conditions. Formation of [4]Al can be elucidated as follows. Probably, Al in compounds in question originates from kaolinite, as this mineral is very frequent in coal. Mentioned Al-complex was formed through the reaction of kaolinitic hexa-coordinated Al with phenols (prevailing oxygen-contaning components in coal substance). During this process the octahedral structure of hexa-coordinated Al was retained, but ligands coordinated around the central Al-atom changed. At first, delamination of a kaolinitic structure through the effect of phenols proceeded and separation of the Al octahedral and silica tetrahedral layers occurred. Then two oxygens in the Al octahedron were substituted with two phenoxide groups while OH groups were preserved. As result, Al-tetrahydroxo-diphenoxide complex was formed. During low temperature ashing this complex was transformed to [4]Al at only 350 °C.

CK:P02 Geopolymerization of Meta-kaolins with Different Morphologies

J. Dedecek, J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic; V. Medri*, S. Fabbri, ISTEC-CNR, Faenza, Italy; Z. Sobalik, Z. Tvaruzkova, J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic; A. Vaccari, Dipartimento di Chimica Industriale e dei Materiali, University of Bologna, Bologna, Italy

The reactivity of two commercial meta-kaolins with similar composition and specific surface areas but different morphologies was tested during geopolymerization with potassium silicate alkaline solution. Manual and short term mechanical stirrings were used to not complete geopolymerization and to emphasize the powders surface reactivity. Moreover, radiation, infra red, micro waves heating were used during curing. The degree of geopolymerization was checked by SEM and N2 adsorption (BET), FTIR and 27Al MAS NMR spectroscopies. The meta-kaolin powder with rounded agglomerates was the less reactive, but it was the more sensitive to the various geopolymerization conditions. The fine dispersed lamellar powder was more reactive and it was mainly affected by mixing. The addition to the potassium silicate alkaline solution of a small alkaline cation such as lithium favoured the dissolution stage during geopolymerization, but decreased the melting temperature.

CK:P05 Chemical and Biological Characterization of Geopolymers for Potential Application as Hard Tissue Prostheses

Michelina Catauro*, Flavia Bollino, Duilio Verardi, Department of Mechanical and Aerospace Engineering, Second University of Naples, Aversa, Italy; Isabella Lancellotti, Elie Kamseu, Cristina Leonelli, Department of Materials and Environmental Engineering, University of Modena and Reggio Emilia, Modena, Italy

In this study different geopolymers have been investigated and characterized as potential biomaterials. The work presents exhaustive FT-IR, SEM/EDS and X-Ray studies of several geopolymer formulations, where water content, water to solid content and curing conditions have been varied during mixing stage, maintaining constant the ratios among Na-Al-Si. The amorphous matrix is typical of sodium aluminosilicates with stretching bands at 950-1250 cm-1 and at 420-500 cm-1. The presence of zeolitic phases has been observed by XRD at the surface of the material. In order to study their bioactivity, samples of the studied materials were soaked in a simulated body fluid (SBF), the bioactivity of the synthesized geopolymers has been showed by the formation of a layer of hydroxyapatite on the surface of the materials.

Symposium CL

REFRACTORIES: RECENT DEVELOPMENTS IN MATERIALS, PRODUCTION AND USE

Oral Presentations

Keynote Lecture

CL:KL **The Federation for International Refractories Research and Education (FIRE): Progress and Outcome on Research, Education and Industrial Partnership**
Michel Rigaud, Professor Emeritus, University of Montreal

FIRE has been incorporated as a non-profit organization, in Canada, in May 2005. It is now a network of professors and researchers, from 8 universities representing 6 nations, who have gathered to focus on well-defined precompetitive research projects, supported by 10 industrial partners, to train high qualified personnel for the industry. The evolution of the refractory education arena in an economically globalized world is presented, with the concept of crowd-sourcing in background. The FIRE realizations are highlighted in such a context.

Session CL-1
Raw Materials

CL-1:IL01 **Reactive Oxide Micropowders and Chemical Additives for Refractory Castables**
C. Parr*, G. Assis, Ch. Wôhrmeyer, H. Fryda, Kerneos S.A., Neuilly sur Seine, France

In recent years, there has been significant growth in the application of self-flow refractory castables which contain reactive oxide micropowders. The rheological characteristics cannot be effectively achieved without the addition of a super-plasticiser or deflocculant. This paper presents a study into additive systems that yield high flow whilst ensuring a rapid acquisition of mechanical strength. The effect of different types and dosages of advanced polymers as well as classical additives is investigated. A variety of techniques were used to quantify early age structure development, exothermic profiles were coupled with ultrasonic techniques to measure the developing structure and this was linked to the hydration steps of the calcium aluminate binder. Specific focus is given to the chemical interactions which control the hardening properties of deflocculated castables and in particular the mechanisms which control the strength development. A technique has been developed to analyse pore solutions through the placing phase and into the hardening period and this provides an initial insight into the interactions between reactive oxide powders and chemical additives and how they can be harnessed to deliver optimal placing and placed properties.

CL-1:IL02 **Synthesis of Carbide Ceramic Powders by Carbothermal Reduction of Organic Precursors**
T. Nishimura*, H. Tanaka, N. Hirosaki, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; S. Ishihara, Nagoya Institute of Technology, Nagoya, Aichi, Japan; J.-S. Lee, Hanyang University, Seoul, Republic of Korea; S.-H. Lee, Korea Institute of Materials Science, Changwon, Gyeongnam, Republic of Korea

Fabrication of two kinds of carbide ceramic powders, silicon carbide and aluminum silicon carbide, was investigated in order to synthesize pure powders. Control of particle size and purity were tried in carbothermal reduction of organic precursors. Fumed silica was used for silicon source and phenolic resin was for the carbon source for silicon carbide in the carbothermal reduction process. Gel-like mixture was obtained by mixing two materials with ethanol. Dried gel-like mixture was heat treated in Ar flow. Silicon carbide phase was formed by heat treatment at 1800 °C. Resulted powders were different in particle size with changing silicon source and carbon source ratio. Al(OH)3, SiO2 and phenolic resin were used for aluminum silicon carbide (Al4SiC4). They were mixed in ethanol and dried in vacuum at 100 °C for 12 h for cross linking. A gel-like material was obtained and used as a precursor. It was heat treated in Ar at 1700-1900 °C. Mono-phase and hexagonal plate-like Al4SiC4 powders were synthesized via carbothermal reduction of the precursor. X-ray diffraction data indicated the orientation of the compacted powders along c-axis due to the stacking of plate-like Al4SiC4 powders. Microscopic observation showed that the synthesized powders were mainly hexagonal platelets. The main synthetic mechanism of the ternary carbide powder during the carbothermal reduction process was gas-solid reaction.

CL-1:IL03 **The Phase Equilibrium Diagrams as a Tool for the Design and Use of Refractories**
A.H. De Aza, Instituto de Ceramica y Vidrio (ICV) - CSIC, Madrid, Spain

Refractories are complex materials used at high temperature, in severely corrosive atmospheres and in contact with aggressive liquids. The high temperatures imply that such systems tend to equilibrium and this is frequently attained during service; at least local equilibrium is achieved. This allows the basic principles of phase diagrams to be used in this technology. Traditionally, refractories has been designed to be close to equilibrium so that in-service changes were restricted. Currently, additions of raw materials are often made that will react in use, in a controlled manner, to give favorable effects under the service conditions. Equilibrium diagrams are valid not only for determining the thermodynamic tendency but also for predicting the final equilibrium state and to know the way through which the material moves into the final state. In this context equilibrium diagrams become a powerful tool for a better understanding of the behavior of refractrories during service. After a general consideration on the importance of phase equilibrium diagrams in this field, criteria for using equilibrium diagrams, as a tool for improving traditional refractories and/or designing advanced or new refractories, will be given. Pertinent examples in different systems will be discussed.

CL-1:L04 **Exploitation of Ceramic Wastes by Recycling in Alumina-Mullite Refractories**
F. Mazzanti*, A. Brentari, A. Coglitore, C. Mingazzini , M. Labanti, M. Scafè, S. Sangiorgi, M. Villa, ENEA, Engineering of Components and Processes Section - Faenza Research Centre, Faenza, Italy; S. Martelli, Centro Sviluppo Materiali S.p.A., Rome, Italy

Alumina-mullite (AM) refractories are widely used as liners in gas turbines for power production, because of their peculiar properties, appropriate for the thermal insulation of combustion chambers, characterized by turbine inlet temperature around 1400 °C. The typical tiles are made with a mixture of alumina and mullite with different granulometries, including a coarse fraction. In this work the feasibility of recycling of ceramic wastes, which come from other industrial processes, into AM refractories was assessed. The ceramic wastes are made up of alumina and silica and nowadays are disposed to landfill. Their exploitation inside AM refractories would produce both environmental and economic benefits. The effects of their addition on phase composition, microstructure and thermomechanical properties of AM refractories were investigated. MOR and Young's modulus were determined at room temperature and up to 1400 °C by four point flexural tests; thermal shock resistance was evaluated by MOR measurements after quenching tests. The comparison with some commercial AM refractories shows that thermomechanical properties and thermal shock resistance were not significantly compromised by ceramic shell additions up to 20%.

CL-1:L05 **Phase Equilibria and Crystal Structures in Ternary Systems Ce, Eu, Yb-VIIIb Group Element-Boron**
O. Sologub*, P. Rogl, Institute of Physical Chemistry, University of Vienna, Vienna, Austria; L. Salamakha, E. Bauer, Institute of Solid State Physics, Vienna University of Technology, ,Vienna, Austria; G. Giester, Institute of Mineralogy and Crystallography, University of Vienna, Vienna, Austria

Proper multicomponent materials' performance demands the profound knowledge on phase formation, crystal structure and phase relations. In a search for interesting physico-chemical properties systematic studies on rare earth (Ce, Eu, Yb) - platinum metal - boron systems have been carried out by X-ray powder and single crystal diffraction. In these systems boride compounds behaviour may be strongly influenced by possible valence instabilities of Ce, Eu and Yb ground states. Phase equlibria in metal rich region in the systems with palladium are governed by formation of perovskite-type compounds RPd3Bx and phases near the composition RPd7B2.5. The systems with platinum exhibit phases structurally related to CaCu5-type and both CaCu5- and Laves phases. Including data on the corresponding nickel containing systems, a comprehensive overview will be given (i) on the structural classification of the rare earth-VIIIb group element-borides and (ii) on the corresponding structure-property relations. Acknowledgement. Research is supported by Austrian National Science Foundation FWF Lise Meitner project M1067-N20.

CL-1:IL06 The Latest Trend in Refractories for Iron and Steelmaking in Nippon Steel Corporation

T. Matsui, Refractory Ceramics R&D Division, Nippon Steel Corporation, Futtsu city, Chiba pref., Japan

The latest trend of the refractory technology in Nippon Steel Corporation is described breiefly. Amid the ever-increasing proportion of high-grade steels and dramatic changes in crude steel output, the company has steadily reduced specific refractory consumption and enhanced and maintained the international competitiveness of its refractory technology by effectively applying the results from development of new refractory materials and new technologies for furnace construction, repair, diagnosis and recycling for the individual iron and steelmaking processes.

CL-1:L08 The Effect of Additives on Performance of Chromite Base Ladle Filler Sands for Continuous Casting

F. Farshidfar, M. Ghassemi Kakroudi*, Sh. Khameneh Asl, Department of Material Science and Engineering, Faculty of Mechanical Engineering, University of Tabriz, Tabriz, Iran

Nozzle filler is a mixture of refractory raw materials and it is used in the nozzle of ladle in continuous casting of steel. The main goal is to achieve a higher level of free opening performance. High free opening rates of ladles are required in steel making to improve steel quality. The use of an oxygen lance for the artificial opening results in product downgrading by steel oxidation. Free opening rate is mainly determined by the performance of the ladle filler sand. Different types of sands are incorporated into the inner nozzle and well block after ladle preheating in order to act as a filler material. Chromite- based sands are one of the most widely used. Several operative variables and materials characteristics affect their in service performance. In this work a set of chromite ladle filler sands selected and we focused on the understanding of the sintering behaviour of the sands under operative conditions. With this aim, samples were shaped and sintered by different thermal treatments for further microstructural and mechanical evaluations and penetration depth. The present work also deals with the effect of different additives such as carbon and feldspar on performance of the sand.

Session CL-2
Testing

CL-2:IL01 Testing Procedures for Postmortem Analyses on Refractories Used in Non-Ferrous Furnaces

G. Oprea*, Materials Engineering, University of British Columbia, Vancouver, BC, Canada

This paper presents the general and particular testing procedures used by the refractories group of UBCeram (Ceramics and Refractories Research and Testing Laboratory) at the University of British Columbia for failure and/or post-mortem analyses on refractories used in non-ferrous smelting, converting and refining furnaces. Selected examples of experimental work are detailed on Flash Furnaces for Ni-Cu and Zn-Pb smelting, Peirce Smith (PS) converters for Ni-Cu matte and Bottom Blown Oxygen Converters (BBOC) for Zn-Pb refining and Pb-Ag cupellation. The general procedures refer to sampling, preparation of the testing specimens and the details of all mandatory and elective tests to be performed, with the specific outcomes to be expected from each particular test and the possible correlations between them. On selected experimental results, the micro structural changes during use were correlated with the physical and mechanical properties of the used and un-used bricks in order to identify the mechanisms of wear. As the penetration and corrosion by the liquid and gaseous environments play decisive roles on the failure or wear, particular laboratory testing methods and experimental set-ups, simulating the industrial conditions, are also presented in a few examples in order to emphasize their role on the total wear during use. An original slag corrosion criterion was used for slag corrosion data processing. Selected experimental results are also presented for hydration, sulphation, penetration and corrosion by Ni-Cu matte, fayalite type slags (NI-Cu and Zn-Pb), erosion by high velocity solid particulates, Boudouard reaction and Kirkendall effect in CO atmosphere and the contribution of complex fumes (Zn, Pb, Cd and Sb) to the mechanisms of wear for magnesia-chrome bricks of burned (B), direct bonded (DB) and rebounded fused-grain (RFG) type.

CL-2:IL02 How to Enhance Strain to Rupture of Refractory Materials for Thermal Shock Applications?

M. Huger[1]*, T. Ota[2], N. Tessier-Doyen[1], T. Chotard[1], P. Michaud[1], [1]Groupe d'Etude des Matériaux Hétérogènes (GEMH), ENSCI, Limoges, France; [2]Nagoya Institute of Technology, Nagoya, Aichi, Japan

This work is devoted to the study of thermomechanical properties of several industrial and model refractory materials in relation with the evolution of their microstructure during thermal treatments. The aim is, in particular, to highlight the role of thermal expansion mismatches existing between phases which can induce damage at local scale. The resulting network of microcracks is well known to improve thermal shock resistance of materials, since it usually involves a significant decrease in elastic properties. Moreover, this network of microcracks can strongly affect the thermal expansion at low temperature and the stress-strain behaviour in tension. Although these two last aspects are not so much documented in the literature, they most probably also constitute some key points for the improvement of the thermal shock resistance of refractories. Evolution of damage during thermal cycling has been monitored by specific ultrasonic devices at high temperature. Beyond its influence on Young's modulus, this damage also allows to reduce the amplitude of the thermal expansion and to enhance the non-linear character of the stress-strain curves determined in tension. The large increase in strain to rupture, which results from this non-linearity, is of prime interest for thermal shock application.

CL-2:L03 Thermo Mechanical Comparison Between SFRC With No Cement and a Similar Ultra Low Cement Castable

A.P. Silva*, D.G. Pinto, T.C. Devezas, Dept. Electromechanical Eng. (CAST), University of Beira Interior, Covilha, Portugal; A.M. Segadaes, Dept. Ceramics and Glass Eng. (CICECO), University of Aveiro, Aveiro, Portugal

In previous works it was demonstrated that a self flow refractory castable (SFRC) of 100% alumina composed by a matrix of fine particles and a commercial aggregate, it can be optimized to obtain simultaneously a high fluidity in fresh paste and high mechanical resistance after sintering. In present work the performing of this SFRC, with no cement, formed by 3 classes of fine particles (two tabular with size less than 63micra and one reactive alumina CT3000SG) and, three commercial classes of tabular alumina as aggregate (from 0.2 to 3.0mm) was compared with another castable, with 1% of aluminate cement (ultra low cement castable), substituting equal percentage of reactive alumina. It was compared the behaviour on properties as the Flowability Index (FI), setting time, weight reduction, linear shrinkage, density, porosity, water absorption, mechanical resistance, thermal shock, packing density in four phases (dry powders, fluid paste, consolidated green body and after sintering). The castables are also characterized by X-ray diffraction, thermal analysis (TG and DTA) and dilatometry. The results shows that the SFRC with no cement presents higher FI, larger setting time, smaller packing density, smaller weight reduction, smaller shrinkage and higher mechanical resistance.

CL-2:L04 Fracture Resistance Investigations of Refractory Materials

George Gogotsi, Pisarenko Institute for Problems of Srength, Kiev, Ukraine

Advanced oxide and nonoxide refractory materials were tested by edge flaking with different standard diamond indenters. Fracture resistance characteristic obtained with the Rockwell indenter (named FR) was calculated from results of direct measurements that did not make use of linear fracture mechanics concepts, which is typical of fracture toughness determinations. It is proportional to the Kc values measured by the single edge V-notched beam (SEVNB) method. The discussed edge fracture (EF) method enables the determination of fracture resistance of ceramics in small-size specimen tests. It has been demonstrated that the EF test method can be quite adequate for enhancing the reliability of comparative fracture resistance estimates and was appropriate for evaluating the uniformity of refractory material items by their fracture resistance. Such tests with small size specimens can be performed on the equipment available in a conventional mechanical laboratory. The EF method may also be employed for studying the localized mechanical behaviour of the material on the edges of the items.

CL-2:IL05 **Standard Testing of Refractories**

X. Buttol, INISMa - Institut National Interuniversitaire des Silicates, Sols et Matériaux, Mons, Belgium; J.-P. Erauw, CRIBC - Centre de Recherche de l’Industrie Belge de la Céramique, Belgium

Refractories cover a wide range of products. With the aim to precisely describe the key product properties, end users and refractory producers have progressively developed a common language: refractory standards. After a brief description of refractory standards history, a synoptic overview will be given on the similarities, discrepancies and global trends in the standards promoted by the national, regional and worldwide standard organisations. Then, we will illustrate standardization opportunities by an example. Our research centre, active both in the field of refractory products and in refractory standards working groups, has launched a pre-normative research in the field of unshaped refractories. It focuses on standard methods to assess the workability and setting of hydraulically bonded unshaped products. Among the investigated methods, the so-called “exothermic profile” has a high potential to become a standard for refractory producers or end users. However, the reproducibility of this method is greatly influenced by operating conditions. Therefore, establishing a standard procedure taking into account a careful control of operating conditions is a necessity.

CL-2:IL06 **Characterisation of the Fracture Path in "Flexible" Refractories**

Harald Harmuth, Chair of Ceramics, University of Leoben, Leoben, Austria

The denomination “flexible” is chosen in the professional jargon of refractories technology for materials able to bear relatively high strains without or with acceptable loss of strength. In many cases this term is equivalent to relatively low brittleness. Characterisation of brittleness based on fracture mechanical investigations may use figures-of-merit like brittleness numbers, a so called characteristic length or the R’’’’ parameter according to Hasselman. In many cases these figures show that brittleness reduction of refractories is achieved by decrease of strength with at the same time more or less unaffected specific fracture energy. Microscopic investigations of fracture paths aim to exhibit which peculiarities of the microstructure enable this change of mechanical properties. A microscopical technique developed for this purpose separately evaluates the relative crack lengths along the grain/matrix interface, within the matrix and within the grain. Results obtained for several types of refractories show brittleness decrease is associated by an increase of the relative crack length along the grain/matrix interface and a decrease of transgranular fracture. Prefabricated microcracks and a relatively low grain/matrix bond strength may support this type of crack propagation.

CL-2:L07 **Mechanical Evaluation of Al2O3-MgO-C Refractory Bricks by Stress-strain Curves**

V. Munoz*, A.L. Cavalieri, A.G. Tomba Martinez, División Cerámicos - INTEMA, Mar del Plata, Argentina

The increasing demand for Al2O3-MgO-C refractory bricks in the steel-making industry is due to their high performance under the more and more severe operating conditions (higher temperatures and mechanical loads, thermal gradients and interaction with slag, gases and solid particles). However, the material damage is unavoidable, being imperative the knowledge of thermochemical and thermomechanical properties in order to improve the material design in view of increasing the lifetime and reducing both the costs and the environmental impact. In this work, the high temperature mechanical behavior of two commercial Al2O3-MgO-C bricks of steel-making use was evaluated by stress-strain curves. Uniaxial compression tests of cylinders were performed at temperatures from RT to 1350°C in controlled atmosphere. The stress-strain curves were obtained using a servo-hydraulic machine with a high stiffness load frame (INSTRON) and an axial capacitive extensometer (+/- 0.6 micron) suitable for high temperature measurements. The tests were performed in displacement control (0.1 mm/min) up to the specimen failure. From the curves, mechanical parameters were determined: fracture strength and strain, and Young’s modulus. After test, several complementary techniques were used to analyze the main microstructural and compositional changes. The mechanical properties were analyzed in terms of both the refractory composition and microstructure and the changes occurred with temperature during the tests.

CL-2:L08 **Resistance Parameters During Water Quench Test of Low Cement Castable**

S. Martinovic, M. Vlahovic, Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia; J. Majstorovic, University of Belgrade, Faculty of Mining and Geology, Belgrade, Serbia; T. Volkov-Husovic*, University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

Over the last decades, use of monolithic refractories has been increasing greatly because of their significant advantages over other shaped refractories of the same class. Among the unshaped refractories, the refractory castables are one of the most important groups of these materials due to their superior technical and economical characteristics. The low cement high alumina castable studied in this paper was synthetised, cured, and then sinetered at 1300 °C for 3 hours. Behavior of the low cement castable during the thermal shock testing was the aim of investigation. The water quench test was chosen as the most popular experimetal method for thermal stability testing. Implementation of non-destructive methods, such as image analysis and ultrasonic measurements, were used in order to monitor thermal shock behavior of the samples during testing. Fracture (R and R’) and damage (R’’’ and R’’’’) resistance parameters were calculated using measured and calculated thermal and mechanical properties. Resistance parameters showed very good correlation with the number of water quench test. Obtained results pointed out that the low cement castable exhibited excellent thermal shock behavior, measured by 110 cycles of water quench test.

CL-2:IL09 **The Fracture Toughness of Refractories**

Richard C. Bradt, The University of Alabama, Tuscaloosa, AL, USA

The fracture toughness of refractories, KIC, is addressed first on a stress intensity basis and then on an energy basis. For the latter, the energies for crack initiation and propagation are separated using the R-Curve concept. The energies are compared with the thermodynamic surface energies of the materials. The energy differences are then related to the role of the microstructure in the fracture process and their contributions to the R-Curve as it reflects the energy for crack propagation. The importance of these differences is related to the individual mechanisms which contribute to the rising R-Curve of refractory materials. The relation of this concept to thermal shock damage resistance is presented.

CL-2:IL10 **Thermomechanical Characterisation of Monolithic Castables**

T. Cutard*, N. Donval, A. Mazzoni, C. Michel, Toulouse University, Mines Albi, Research Center on Tools Materials and Processes (ICA-CROMeP), Albi, France; F. Nazaret Aurock, MDI, ZA Albitech, Albi, France

This paper deals with the characterisation of the thermomechanical behaviour of monolithic castables in a wide temperature range, up to 1200 °C. Different test types are considered : tensile tests, compression tests, bending tests and tests on more complex shapes and geometries. A particular attention is paid to the detailed characterisation and interpretation of the non-linear behaviours of these materials. Monotonic, cyclic and creep tests ate considered. In some cases, digital image correlation (DIC) methods can be coupled to mechanical tests to obtain strain fields. Such results are particularly interesting to observe and to understand damage processes. As damage is a major characteristic of the monolithic castable behaviours, linked are established between the thermomechanical behaviour and damage mechanisms. Two main scales are taken into account for damage characterisation : the macroscopic and the microscopic ones. Main mechanims that are considered deal with microcracking, macrocracking, debonding, and cavitation. Two types of materials are considered: non-reinforced and fibre reinforced refractory castables. Behaviour specificities of reinforced materials are discussed too.

CL-2:L11 **Electrical Characterization of Alumina-Based Bodies Containing Al-Rich Anodizing Sludge**

M.J. Ribeiro[1], J.A. Labrincha[2], [1]UIDM, ESTG, Polytechnique Institute of Viana do Castelo, Viana do Castelo, Portugal; [2]Ceramics and Glass Engineering Department, CICECO, University of Aveiro, Aveiro, Portugal

Al-rich sludge produced from industrial anodising and surface treatment processes had been tested in the fabrication of alumina-based materials, by using unidirectional dry pressing as shaping technique. A mixture from 50 to 50 wt.% of as received Al-anodising sludge and 1400ºC pre-calcined material were prepared in order to achieve interesting final fired refractory and/or electrical insulating materials. Microstructural changes upon sintering and crystalline phase evolution are detailed and their relationship with the electrical behaviour is also studied, by the use of impedance spectroscopy. Finally, different models were used to fit the experimental electrical resistivity values and to estimate the percolation limit of the bi-phase material.

CL-2:L12 High Temperature Mechanical Behaviour of MgO-$CaZrO_3$-based Refractories for Cement Kilns

C. Baudín*, P. Pena, Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain; A. Obregón, J.L. Rodríguez-Galicia, CINVESTAV, Unidad Saltillo, Coahuila, Saltillo, Mexico

The mechanical behaviour of ceramic refractories formulated in the MgO-CaO-SiO_2-ZrO_2 system is analysed. Materials have been designed taking into account the phase equilibrium relationships to obtain MgO-$CaZrO_3$-Ca_2SiO_4 or MgO-$CaZrO_3$-Ca_3 $Mg(SiO_4)_2$ as final crystalline phases. Different relationships between the proportion and sizes of the fines and the aggregates have been explored. The microstructure of the materials has been characterised in terms of density, crystalline phases and phase distribution and morphology. A combination of X-Ray diffraction (XRD) analyses and Reflected Light Optical Microscopy has been used. The relationships between the obtained phases and microstructures and the grain size distributions of the used raw materials have been established. The room temperature dynamic Young´s modulus has been calculated from the natural vibration frequency of bars tested in flexure by impact. Static Young´s modulus and strength have been evaluated by three points bending at room temperature and 1100 °C. The relationships between the mineralogical composition and the obtained microstructure and the mechanical behaviour have been established.

Session CL-3
Manufacturing, Selection, Design and Use

CL-3:IL01 Carbon Containing Castables and More

C.G. Aneziris, S. Dudczig*, Institute of Ceramic, Glass and Construction Materials, Technische Universität Bergakademie Freiberg, Freiberg, Germany

Carbon containing castables play today a key role in refractory lining applications as well as in preformed products in the ferrous and non ferrous industries as well as in chemistry applications. This work explores formulations and properties of carbon containing castables with and without cement binder systems as well as a new multifunctional resin binder, that contributes as flowing agent and binder system. Due to the fact, that no impurities are incorporated in the matrix during operation very good thermomechanical properties are achieved as well as flexible workability in advance. This binder system can be modified and applied also in carbon free castables.

CL-3:IL02 Microtexture Control of Alumina Using Anisotropic Alumina Particles

Shinobu Hashimoto*, Sawao Honda, Yuji Iwamoto, Nagoya Institute of Technology, Nagoya-shi, Japan; Hirofumi Hirano, Towa Refractory Engineering, Kani-shi, Japan

Anisotropic alumina particles, namely alumina platelets were obtained by heating a powder mixture consisting of γ-Al2O3 : Na2SO4 = 1:3 (molar ratio) at 1100 °C for 1 h. This γ-Al2O3 was beforehand prepared by heating the Al4(SO4)3·14~18H2O at 900 °C for 3 h. The shape of the formed alumina platelets was 5-10µm in diameter and 5-10 in aspect ratio. One of our research topics was fabrication of porous alumina body with high porosity and mechanical properties using the platelet alumina particles. When the powder mixture consisting of 85% of alumina platelets, 10% of fine alumina and 5% of corn starch was uniaxially pressed at 1 MPa and heated at 1400 °C, porous alumina with 75% relative density was formed. Its compressive strength was 0.8 MPa. In an attempt to increase the compressive strength of the porous body, magnesium nitrate solution treatments were performed, followed by reheating to 1400 °C for 1 h. When 0.1 mol/l magnesium nitrate solution was used, the compressive strength of the porous alumina increased to 1.7 MPa, retaining the relative density of 27%. The other topic was fabrication and mechanical properties of dense alumina body with layered microstructure based on alumina platelets using a PECS (Pulse Electric Current Sintering) technique. Mechanical properties such as bending strength and fracture toughness and thermal conductivity of the dense alumina body show different values in parallel and perpendicular direction of pressing by PECS.

CL-3:L03 Application of Organic Thickening Agents to the Rheology Study of Ceramic Slurries Used in the Investment Casting Process

J. Ferenc[1]*, H. Matysiak[2], J. Michalski[3], K.J. Kurzydlowski[1], [1]Faculty of Materials Eng., Warsaw University of Technology, Warsaw, Poland; [2]University Research Centre “Functional Materials”, Warsaw University of Technology, Warsaw, Poland; [3]Materials Engineers Group Sp. z o.o., Warsaw, Poland

The paper presents results of the study on the influence of rheology modifiers on ceramic slurries used in the investment casting processes. The ceramic slurries used in the study were based on zirconium silicate in silica sol binder. Following modifiers were used as thickening agents: carboxymethyl cellulose LV and S, locust bean gum and xanthan gum. The thickening agents were pre-tested with a silica sol binder before testing with ceramic slurries. The viscosity measurements were carried out with the use of Brookfield rheometre and in semi-industrial scale using Ford cup and plate test. Results of the study demonstrate the potential of employing the substances selected as thickening agent as rheology modifiers for ceramic slurries used in investment casting process.

CL-3:L04 Adding Borates to Al2O3-MgO Refractory Castables

M.A.L. Braulio*, V.C. Pandolfelli Federal University of Sao Carlos, Materials Engineering Department, Materials Microstructure Engineering Group - GEMM, Sao Carlos, SP, Brazil

The composition of in situ spinel-forming castables comprises fine dead-burnt magnesia and reactive alumina in order to form magnesium aluminate spinel (MgAl2O4) at temperatures above 1200 °C. Considering the expansion behavior associated with this reaction, small amounts of microsilica are generally added in order to generate a liquid phase which can counterbalance the expansion by a softening mechanism. Nevertheless, as these castables are bonded with calcium aluminate cements, low-melting point temperature phases can result and lead to refractoriness drawbacks. Considering these aspects, novel transient liquid phases were evaluated by adding two different borate sources. The B2O3 addition is a well-known technology applied to pre-formed spinel synthesis in order to increase the reaction formation rate and, therefore, can speed up the spinel and calcium hexaluminate (CA6) formation during the alumina-magnesia castables’ sintering. As a consequence, faster spinel and CA6 took place when using these borate sources. Additionally, better creep resistance and hot modulus of rupture were attained when compared to the microsilica-containing composition, pointing out a novel engineered route for advanced alumina-magnesia refractory castables.

CL-3:L05 Sintering Studies on Magnesia-Rich Chromium-Free Spinel-Bonded Basic Refractories

R. Lodha*, C. Oprea, T. Troczynski, G. Oprea, Department of Materials Engineering, University of British Columbia, Vancouver, BC, Canada

Basic bricks with Cr_2O_3 from chrome ore, as the spinel forming oxide, are used in the non-ferrous industry because of their corrosion resistance against fayalite-type slags, rich in FeO. Our objective in this study was to replace Cr^{3+} with Me^{4+} ions, which along with Fe^{3+} could maintain the spinel formation capability with MgO and perform similarly against fayalite slags in non-ferrous furnaces. Our preliminary research studies showed that Cr-free spinels in the MgO-Al_2O_3-FeO_x-$Me^{4+}O_2$ systems could perform against fayalite slags similar to the complex $(Mg^{2+}, Fe^{2+})O\cdot(Cr^{3+}, Fe^{3+}, Al^{3+})_2O_3$ spinel, the main corrosion resistant component in the magnesia-chrome bricks. The incorporation of iron oxide in the MgO-Al_2O_3-$Me^{4+}O_2$ systems would contribute to reactive sintering and also in decreasing the solubility of both the ferrous and ferric ions present in the fayalite slag. Phase analysis on stoichiometric mixes showed that the use of tetravalent cation oxides like tin dioxide (SnO_2) and titanium dioxide (TiO_2) can induce high solubility of spinel in magnesia. In order to maintain charge balance, two trivalent cations were replaced by a tetravalent and a bivalent cation causing the additional bivalent cation to occupy the octahedral position thereby creating an inversion in position of the bivalent ions similar to the behavior exhibited by Fe^{3+} occupying tetrahedral site in complex spinel phase of magnesia-chrome ceramics. Most of the magnesia-chrome refractories have ~60 wt. % MgO and hence our experimental mixes contained that amount and called “magnesia-rich” compositions, to be distinguished from the stoichiometric $MgAl_2O_4$ spinel. Our findings showed that the incorporation of nano TiO_2 powders reduces the temperature of spinel formation as the diffusion path is shortened and thus activates both synthesis and sintering. Compositions containing 60 wt. % magnesia with alumina, nano TiO_2 and Fe_2O_3 fired below 1500 °C for 3 hours resulted in complete spinel formation and open porosity less than 5%.

CL-3:IL06 **Analysis and Interpretation of Liquid Oxide Corrosion Microstructure**

Jacques Poirier, CNRS-CEMHTI and University of Orléans, France

Corrosion by liquid oxides is one of the most severe modes of degradations which limit the lifetime of the refractory linings. The study of the microstructures of corroded refractories provides essential information. However, the interpretation of the microscopic observations is difficult: - The refractories are multi-component and heterogeneous ceramics, - The microscopic observations are carried out at room temperature. They are not representative of the mineral and vitreous phases existing at high temperature, - During cooling, new solid phases appear by crystallization of liquid oxides. The composition of the vitreous phases also evolves with the temperature. Consequently, the information obtained is often limited. In this lecture, we will present a method to analyse and interpret the microstructures of refractories after use. The concept of local thermodynamic equilibrium and the use of the phase rule make it possible to interpret the microstructures of corroded refractories, to explain the observed mineral zonation and to quantify the composition of the liquid phase at high temperature from chemical profiles established by S.E.M. Experimental data from corrosion of SiC, MgO-C, high alumina refractories will illustrate and validate this theoretical approach.

CL-3:IL07 **Aluminum Titanate Refractories for Molten Aluminum**

Y. Ohya, Gifu University, Gifu, Japan

Aluminum titanate (AT) ceramic has a very low, sometimes negative, thermal expansion coefficient and therefore high resistance against thermal shock. This is caused by grain-boundary cracks due to large thermal expansion anisotropy of AT. Because of the high thermal shock resistance, AT ceramic is considered to be applied to refractory in aluminum die casting industry. Thermal shock resistance and mechanical properties of AT ceramics are conflicting properties and an optimization of the microstructure is essential. Another important aspect is chemical reaction with molten aluminum at operating temperatures. The Ti4+ ion in the AT ceramics is reduced by aluminum to form metallic Ti and aluminum oxide. Recently a role of the grain-boundary crack opening in the corrosion by molten aluminum is realized. The grain-boundary crack opening in AT ceramics at operating temperature should be controlled to avoid severe corrosion by molten aluminum. Moreover effects of some additives and surface coatings on the corrosion are very interesting to fabricate high resistant AT ceramics. Here the properties of the AT ceramics as a refractory for molten aluminum and their grain-boundary cracks are reviewed.

CL-3:L08 **Interactions Between Superalloys and Mould Materials for Investment Casting of Turbine Blades**

F. Valenza*, IENI-CNR, Genova, Italy; R. Nowak, N. Sobczak, Foundry Research Institute, Krakow, Poland; A. Passerone, IENI-CNR, Genova, Italy; M. Di Foggia, Europea Microfusioni Aerospaziali, Morra De Sanctis, Italy; M.L. Muolo, IENI-CNR, Genova, Italy

The need of increased efficiency of industrial gas turbines comes also through the improvement of the composition of superalloys (addition of new solutes) and of the manufacturing technologies involved in the investment casting process of the turbine blades. Thus, the knowledge of the interactions between these ceramic materials and the molten superalloys must be deepened in order to minimize the formation of internal defects, to improve the casting surface and to optimize finishing and casting operations. In this work, a study of the wetting behaviour of some Ni or Co based superalloys, used for the fabrication of turbine blades, has been performed with reference to the interactions of these alloys in the molten state with the silica-aluminate based ceramic materials forming the shell or the core in the casting process. Wettability tests have been performed by means of the sessile drop method at 1500 °C; the characterization of the interfaces between the molten drop and the substrates has been made by SEM/EDS analysis to check the final characteristics of the solidified interfaces. The results are discussed in terms of chemical interactions in relation to the processing parameters and as a function of the surface and interfacial energetic properties of the systems.

CL-3:L09 **Effect of Grain Boundary Cracks on Corrosion Behavior of Aluminum Titanate Ceramics in Molten Aluminum Alloy**

M. Tanaka*, K. Kashiwagi, N. Kawashima, S. Kitaoka, Japan Fine Ceramics Center, Nagoya, Japan; O. Sakurada, Y. Ohya, Gifu University, Gifu, Japan

Aluminum titanate (Al2TiO5: AT) ceramics exhibit excellent thermal shock resistance and insulation efficiency because of a very large thermal expansion anisotropy, which leads to grain boundary cracking during the cooling stage after sintering. Therefore, AT ceramics are attractive as candidate materials for ladles and stokes for Al casting, where these parts are required to have high thermal shock resistance and chemically stability in molten Al alloys. It is well known that the grain boundary cracks in AT ceramics close with rise in temperature, eventually crack-healing. The crack closing temperature strongly depends on AT grain size. However, effect of the grain boundary cracks on the corrosion behavior of AT ceramics in molten Al alloy has not been understood. In this study, the corrosion mechanism of AT ceramics in molten Al alloy containing a slight amount of Mg was evaluated thermodynamically using AT ceramics with greatly different average grain size. At the contact surfaces of the ceramics with the molten alloy, MgAl2O4 was formed by reduction of AT grains, followed by reaction of produced Al2O3 with Mg dissolved in the alloy and dissolution of Ti. At the opened crack surfaces which were not in contact with the molten alloy, MgAl2O4 and Al-Ti compounds were formed by reaction with Mg evaporated from the alloy. These results reveal that crack-closing improves the corrosion behavior of AT ceramics in molten Al alloy.

CL-3:L10 **Interaction Between CaZrO3 Ceramic and Titanium Alloys Melt**

Chonghe Li*, Yonghui Gao, Xionggang Lu, Weizhong Ding, Zhongming Ren, Kang Deng, Shanghai Key Laboratory of Modern Metallurgy & Materials Processing, Shanghai University, Shanghai, China

The CaZrO3 complex oxide ceramic was synthesized in the development of a potential refractory for melting of titanium alloy. The crucibles (ϕ40X40mm) and the samples (3×4×36 mm) were prepared by solid state sintering of mixture of powder (CaO:ZrO2 =1:1) with a small amount of TiO2 as additive at 1750 °C. The melting of TiNi and Ti6Al4V was carried out in an inducting furnace under vacuum or/and Ar atmosphere for 5 minutes at about 1750 °C. The interfacial reaction between alloys melts and CaZrO3 refractory was investigated by scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS). It is found that the bending strength of CaZrO3 refractory is 36.45MPa, the thickness of interfacial reaction layer is approximately 30-70 µm, and that there are few elements such as Ca, Zr, Ti, and Ni diffused through the interfacial reaction layer. These results may provide the basis for designing a novel refractory for melting of titanium alloys.

CL-3:IL11 **Engineered Expansion Design of in situ Spinel Castables**

M.A.L. Braulio, V.C. Pandolfelli*, Federal University of Sao Carlos, Materials Engineering Department, Materials Microstructure Engineering Group - GEMM, Sao Carlos, SP, Brazil

Alumina-magnesia refractory castables show an expansive behavior as a consequence of the in situ spinel formation. Due to this feature and difficulties to accommodate the volumetric change, thermal shock resistance would benefit from some expansion as a consequence of the resulting compressive stress in the refractory castable. Conversely, a huge expansion could lead to cracks and spoil the above mentioned properties. Considering these aspects, the expansion design of this composition is essential to attain high performance castables. Therefore, this work addresses the road-maps to control the expansion by previous microstructure engineering. One of the alternatives is to select the binder sources, due to the CA6 formation and shrinkage related to hydratable alumina. Furthermore, as microsilica influences the spinel and calcium aluminate formation, selecting its suitable content is another option to forecast castable expansion. Changing the MgO and the Al2O3 grain sizes is an additional possibility, as their particle size reduction led to a lower overall expansion.. By the analyses of these variables, various expansion routes can be attained, resulting in a greater flexibility design for the optimization of the thermal-mechanical benefits when in situ spinels are applied.

CL-3:IL12 **Novel Refractory Development for Synthetic Rutile Manufacture via the Becher Process**

N.A. Stone*, CSIRO Process Science & Engineering, Melbourne, Victoria, Australia; W.W. Wright, Rio Tinto, Melbourne, Victoria, Australia; M. O'Byrne, S. Bow, Iluka Resources Pty Ltd, Geraldton, Western Australia, Australia

Australia is fortunate in that it has ~80,760 kt (Ti equivalent) representing 15% of the world's titanium resources in the form of ilmenite, rutile, anatase and leucoxene. Although of late the annual quantity of mined material has reduced due to the global financial situation, the average amount of material mined was of the order of 700 kt (Ti eq). To date the most common process used for beneficiating the ilmenite in Australia has been the Becher process to produce synthetic rutile of the order of

92-96% TiO_2. Due to the nature of the mineralogy of the deposits, a very small amount of naturally occurring radioactive materials (mainly thorium) is present which for some applications is considered unacceptable. Consequently a number of years ago the Synthetic Rutile Enhancement Process (SREP) was developed which removes the thorium contamination through the use of a boron containing mineral additive which complexes the radioactive material during the reduction process. Unfortunately the consequences of this reaction is the build up of a flux-like material on the walls of the rotary kilns leading to significantly reduced throughput and even significant refractory loss. The aim of this paper is therefore to describe the development of a novel refractory castable system utilising the in-situ formation of aluminium titanate which in combination with matrix chemistry control and thermo-mechanical property design, greatly inhibited the adhesion of process flux on the refractory walls. The development strategy and subsequent history from simulated laboratory testing and early small scale trials up to the performance of the novel refractory in a fully lined kiln operating over a number of years will be highlighted.

CL-3:IL13 Nanostructured Refractories: Current Situation and Future Prospects

Shaowei Zhang, Department of Engineering Materials, The University of Sheffield, Sheffield, UK

This presentation will review the main work so far on nanostructured refractories. It will comprise three main parts. In the first part, several fundamental issues related to the application of nanotechnology in the refractories field will be addressed, including, e.g., 1) why do we need to develop nanostructured refractories? 2) How can we use nanotechnology to tackle the problems in the refracories field? and 3) Is it feasible to use nanotechnology in the refractories industry?. In the second part of the presentation, several important examples of application of nanotechnology in the refractory brick and castable systems will be given and discussed in detail. These examples include the use of nanotechnology to: 1) reinforce current bricks and castables; 2) develop low carbon carbon-containing refractories, and 3) develop carbon containing refractory castables. In the final part of the presentation, the future prospects will be discussed.

CL-3:L14 Novel Basic Carbon Slidegate Refractory for Ca-treated Steel Application

Alireza Rezaie, Mark Snyder, Priyadarshi Desai, Mariusz Ziemnicki*, R&D Dept. Vesuvius Research, Pittsburgh, PA, USA

Slide gates are used to control the flow rate of molten steel in continuous casting. The properties that are important for designing a slide gate refractory are chemical corrosion, thermal shock and abrasion resistance and strength. However, operating conditions and in particular steel chemistry vary by shop and require development of different refractory qualities. Alumina-carbon refractories are the prevalent family for slide gate application due to their superior thermo-mechanical properties. However, they suffer from extensive corrosion in applications that cast calcium treated steel. On the other hand, magnesia based refractories show promising corrosion resistance in this application, but they are poor in terms of thermal shock and abrasion resistance. A novel approach using material based solutions was employed to utilize a combination of properties of both refractory families. This approach resulted in a new product that jointly exhibits thermo-mechanical properties and abrasion resistance of alumina and corrosion resistance of magnesia. This paper will present the properties and key limiting factors. Field results will be discussed as well.

Session CL-4

System Modeling, Simulation and Failure Analysis

CL-4:IL01 Thermal Shock Criteria of Refractory Ceramics: Limitations of Conventional Analyses and Some Numerical Approaches to Improve the Prediction of the Resistance to Thermal Shock

Nicolas Schmitt, LMT Cachan (ENS de Cachan, CNRS, UPMC), Cachan, France, also at IUFM de Créteil (UPEC), Saint Denis, France

Significant advances in mechanical design of ceramic parts were realized with the pioneer works of Kingery and Hasselman. But it seems that for refractories, the use of these criteria becomes now more and more delicate because the limit of the validity of the criteria is probably almost reached. In the first part of the presentation, after a short review of thermal shock criteria, we will underline how they helped to improve the global performance of ceramics and we give some comments on their limitations for refractory materials. In the second part, first we will show how the numerical tools can be useful for the design of refractory structures at high temperatures through several approaches we have developed for refractory structures. One approach is based on a multiscale homogenization to predict the resistance of heterogeneous refractories. Improved thermal shock resistance criteria are proposed accounting for the composition of the material. Then the thermal shock resistance of a nozzle is analyzed by finite element method assuming the material is heterogeneous and using a two-scale approach or it is homogeneous at a macroscopic scale with a non linear behavior. Both analyses point out complementary information useful for the design of the nozzle.

CL-4:IL02 A New Generation of Refractories to Enable Gasifier Fuel Flexibility

James P. Bennett*, Kyei-Sing Kwong, Hugh Thomas, Rick Krabbe, Jinichiro Nakano, National Energy Technology Laboratory; Albany, OR, USA

Gasification is used by industry to convert low cost carbon into materials for producing electricity and chemical products such as fertilizer, plastics, and Fischer-Tropsch liquids. It is considered a critical technology in the success of the DOE's Near Zero Emissions Advanced Fossil Fuel Power Plants, could play a key role in defining long-term energy security in both power and liquid fuels, and is considered a leading candidate for H_2 production in a hydrogen based economy. Slag originating from mineral impurities in the carbon feedstock is of the most concern to slagging gasifier operation, with some gasifiers generating over 100 tons per day of liquid slag. The liquid slag attacks and wears away the internal lining of the gasifier vessel by two major mechanisms, chemical dissolution and spalling. The main component in a refractory lining is chrome oxide. NETL is currently developing a new generation of refractory materials as an alternative to the high chrome oxide refractories currently used, with the goal of improving performance and providing a predictable service life. A number of refractory compositions are being evaluated containing chrome and non-chrome oxide materials through laboratory testing and the use of thermodynamic modeling. Causes of failure and the results of testing candidate refractory materials will be discussed. Thermodynamic will be used to explain phases formed at the refractory/slag interface of worn materials. Field testing has confirmed the promise of at least one material as a next generation gasifier liner.

CL-4:IL03 Modelling of Joint Effect in Refractory Structures

E. Blond[1]*, A. Gasser[1], M. Landreau[2], T.M.H. Nguyen[1], [1]Institut PRISME, Polytech' Orléans, Orléans, France; [2]CPM, Parc d'Activités Forbach Ouest, Forbach, France

To account for joint effect in large structures, two different approaches are possible: the first one leads to model each brick and joint with their own behaviour, the second pleads for replacing them with a homogeneous equivalent material. The homogeneous approach seems to be the most accurate for large structures. The homogenisation approach requires four steps: firstly the definition of a representative spatial arrangement of bricks and joints, secondly the definition of the behaviour of each part, thirdly the choice of constitutive equations for the equivalent homogeneous material and finally the identification of the equivalent material parameters. The main difference between the numerous recent works concerns the definition of the behaviour of joints. The dominant idea is that the non-linear behaviour of mortar (or contact for mortarless joints) is the key point of the structure behaviour. In the present work, the joint is purely elastic but can be closed (perfect joint) or open (broken joint) without any other refinement. Then, the constitutive equation of equivalent material is linear elastic with different joint states. This approach is first used for mortarless masonries. The obtained equivalent behaviour is then used to simulate a bi-axial compression test.

CL-4:L04 Nozzle Wear Mechanisms Developed by Contact with Slag and Steel During Casting Process

V. Peirani, L. Santini, E. Benavídez, E. Brandaleze*, Departamento de Metalurgia, Facultad Regional San Nicolás, Universidad Tecnológica Nacional, San Nicolás, Argentina

It is well known that wearing of submerged entry nozzles (SENs) has a strong impact on the continuous casting process because it can limit the number of heats per sequence and eventually, may induce quality problems in the cast product. The characterization of nozzle wearing is necessary in order to identify the different mechanism and predict nozzle cracks or breakages. In this work, a comparative study on a post mortem nozzle and other one without use is presented. By different techniques of microscopy, XRD diffraction and wall thickness profile measurements, nozzle wear mechanisms were identified. Static and dynamic corrosion tests were carried out to corroborate the post mortem study. The results permit to evaluate the graphite consumption, the oxides grains degradation and the slag penetration grade. To increase the knowledge on the complex corrosion phenomena, physical properties on mould fluxes samples and surface tension measurements were realized.

CL-4:L05 Simulation of Moulding of Refractory Bricks

Dietmar Gruber*, Harald Harmuth, Chair of Ceramics, University of Leoben, Austria

Simulations presented here aim to show reasons for undesirable product heterogeneity and possible defects. Potential negative influences are for example insufficient deaeration, friction between the brick material and the mould, deformation of the mould and an inappropriate mould filling. In a first step data were collected from a production process. This includes the load and displacement during moulding and the mass of the mix filled into the mould. Furthermore the mix permeability in dependence of compaction was measured. For the Finite Element modelling with ABAQUS the brick material was simulated with a Drucker-Prager model including the cap. In this model the cap specifies the hardening along the hydrostatic compression; shear failure is modelled with cohesion and friction angle. The results show the influence of the friction between mix and mould and the permeability on the densities of the green brick as well as the stresses in unconstrained green bricks.

CL-4:L06 Sizing of a Refractory Castable Gas-burner Using Thermo-mechanical Simulations

F. Nazaret[1]*, T. Cutard[2], O. Barrau[1], [1]AUROCK Pépinière Albisia, Albi, France; [2]Toulouse University, Mines Albi, Research Center on Tools Materials and Processes (ICA-CROMeP), Campus Jarlard, Albi, France

Damage is a crucial characteristic of refractory castables and has to be considered to simulate correctly the behaviour of refractory structures. But, damage modelling by finite element simulations remains difficult. Indeed, the use of a continuum damage model with softening leads to strain localization phenomena. Numerical results depend on the mesh. Several numerical methods allow to solve this meshing dependence by introducing an internal length in the material constitutive laws. In this paper, a regularization method has been applied with the Mazars's damage model, considering a scalar value for damage. The considered approach consists in using a regularization of equivalent strain, which is the damage criteria in the model, by a non-local method introducing an internal length. Thermomechanical simulations are performed with this model to predict damage in a gas-burner. The damage level is evaluated after a thermal simulation generating high temperature gradients. Interests to take into account damage in the refractory structures are discussed. Sensitivity of results to material properties are studied. This work gives an example of using thermomechanical simulations to improve the design of refractory castable structures and to help in the material choice.

CL-4:L07 Effect of Joint Condition and Friction Force on Thermal Stress Analysis of BOF

Yuta Hino*, Slag and Refractories Dept., Steel Research Laboratory, JFE Steel Corporation, Chiba, Japan; Yoshisato Kiyota, Slag and Refractories Dept., Steel Research Laboratory, JFE Steel Corporation, Fukuyama, Japan; Yoshimitsu Hattori, JFE Sekkei Ltd., Kurashiki, Japan

Thermal stress simulations by the finite element method (FEM) are widely used to analyze refractory damage caused by mechanical factors. Issues studied by FEM simulation of refractories include joint conditions, and friction between refractories. On this study, the effects of joint conditions and friction force on the thermal stress analysis of the refractory lining in the barrel and cone of the converter were investigated numerically. The results are summarized as follows. (1) The friction coefficient between refractories that had various surface conditions was measured. As a result, a maximum static friction coefficient of 0.52 and a dynamic friction coefficient of 0.42 were obtained for the friction working between the surfaces of baked MgO-C refractories. (2) It is necessary to consider friction force in the thermal stress analysis because local abnormal increases in stress occur, corresponding to large displacement of the bricks. (3) The effect of the joint conditions used here, which were contact element, gap element and anisotropy of mechanical property, on the results of calculations of thermal stress by FEM was comparatively smaller than that of friction force.

CL-4:L08 Selection Criteria and Tools for Refractory Materials to be used in Pulverised Coal Combustion Reactors

P. Miceli*, A. Di Donato, U. Martini, Centro Sviluppo Materiali SpA, Rome, Italy

Criteria and tools are presented for the selection of appropriate refractory materials to be used in pulverised coal combustion reactors for the production of electrical energy. One of the main causes of failure of refractory materials is the high temperature corrosion due to chemical attack of the slag formed from the coal ash and possible additives. Selection criteria are based on the phenomena involved in the corrosion mechanism. The developed tools are based on thermodynamics of chemical reactions between oxides systems and permitted to evaluate the classes of materials in terms of chemical corrosion resistance as a function of slag composition and temperature. The effects of the chemical interaction between slag and refractory on the physical and chemical properties of the slag, such as viscosity, melting point, change of composition, solid phase formation, were also investigated. Experimental tests resulted in agreement with the indications obtained from the thermodynamic evaluation. Preliminary evaluation is an important tool for reducing the number of laboratory trials often expensive and time consuming. These chemical aspects are complementary to the engineering plant aspects and must be taken into consideration for a successful realization of the process.

CL-4:L09 Damage of High Zirconia Fused-cast Refractories During Cooling: an XRD and EBSD Study

A. Sibil, T. Douillard, M. R'Mili, N. Godin, G. Fantozzi*, MATEIS, INSA Lyon, Villeurbanne, France

High zirconia refractories present a very atypical structure: a zirconia skeleton made of dendrites surrounded by a glassy phase. During their cooling from high temperatures, these materials undergo two successive phase transformations: cubic to tetragonal and tetragonal to monoclinic. Though it has been emphasized by acoustic emission monitoring that damage during cooling occurs mainly after the second transformation, there is still a lack of data concerning the mechanisms responsible for the observed cracking. This last transformation being of martensitic type and generating for each tetragonal domain three pairs of twins, it can be assumed that the mismatch between them is the source of internal stresses and further damage. In this study, our work focuses on the arrangement of the monoclinic domains. The preliminary determination of the monoclinic thermal expansion coefficients at the crystal-scale has been performed by X-ray diffraction and Rietveld refinement method. It shows an important disparity between the values following the a and c crystallographic axes of zirconia. The analysis of an EBSD map taking into account this disparity enables to link directly the thermal expansion mismatch between twins with skeleton cracking and zirconia / glassy phase decohesions.

CL-4:L10 Investigation of Refractory Corrosion of a Gas-stirred Steel Ladle by Simulation

S. Vollmann*, H. Harmuth, University of Leoben, Leoben, Austria

The present work aims the calculation of the mass transfer coefficient in the slag area of a gas-stirred steel ladle. The mass transfer in dependence on influencing factors like flow rate and gas throw put was investigated. For this purpose computational fluid dynamics calculations were performed. Due to the fact that during refractory corrosion diffusion-controlled mechanisms take place simulations considering diffusion were done. From the resultant concentration of the diffusive component in the slag in dependence on time the mass flux is known. With the help of Fick´s 1st law that describes the diffusive mass flux the mass transfer coefficient may be calculated. From a dimensional analysis followed by a parameter study conducted with the help of computational fluid dynamics calculations a relation for the estimation of the mass transfer in the slag bath area of the gas-stirred steel ladle was deduced.

CL-4:L11 Constitutive Equations for Creep of Cement Bonded Alumina-Magnesia Refractory Castables with Different Microsilica Contents

A.G. Tomba Martinez[1]*, M.A.L. Braulio[2], V.C. Pandolfelli[2], [1]Materials Science and Technology Research Institute (INTEMA), Ceramics Division, Argentina; [2]Federal University of São Carlos, Materials Engineering Department, Materials' Microstructural Engineering Group (GEMM), Brazil

Alumina-magnesia castables commonly include microsilica in their composition, due its ability to promote better flowability, to inhibit the MgO hydration during curing and drying and to compensate the expansion related to *in-situ* spinel formation. Therefore, the control of microsilica content stands for a way to design the castable expansion based on microstructural engineering. The presence of microsilica promotes the formation of a viscous phase at high temperature which, beside its effect on the spinel and CA$_6$ formation, affects the deformation ability of the castable. This fact impacts straight in the thermomechanical properties such as creep. In this work, the effect of microsilica on the creep of alumina-magnesia castables were analyzed as a function of the additive content (0-1 wt.%). Cylindrical specimens were prepared according to the 51053 DIN standard and fired at 1550 °C for 24 h before testing. Tests were performed in a creep in compression equipment (RUL/CIC Model 421E, Netzch, Germany) at 1450 °C for 24 h under a load of 0.2 MPa. Experimental curves were fitted using the θ-methodology to obtain constitutive equations and creep parameters. A non-linear regression method was employed and a very good fitting of creep strain data (R^2 > 0.99) was obtained. The creep parameters (θ_1, θ_2 and $\theta_3\theta_4$) were correlated to microsilica content and the dominant deformation mechanism operating in the systems.

Poster Presentations

CL:P01 Thermal Shock Behavior of Zircon Based Refractories

N.M. Rendtorff; G. Suarez; Y.L. Bruni; L.B. Garrido; E.F. Aglietti*, CETMIC, Centro de Tecnología de Recursos Minerales y Cerámica (CONICET La Plata-CIC), M.B. Gonnet, Provincia de Buenos Aires, Argentina

In service refractory materials are submitted to local temperature gradients that originate thermal stresses causing a thermal shock (TS) damage to the material. Practical tests for evaluating the thermal shock resistance (TSR) determine the variation or change of some characteristic property of the test sample like E (elastic module) or the strength before and after quenching. In this work, the microstructure and thermal shock behavior of zircon based refractories are analyzed. Several compositions (ten), from pure zircon to 30 % of zircon in a high alumina refractory were studied. The main structural and mechanical properties of the refractories were characterized, as modulus of rupture, elastic modulus, porosity, and microstructure. The dynamic elastic modulus E of the refractories was measured by the excitation technique. The TS behavior was evaluated by measuring the decrease in E and the modulus of rupture, before and after a quenching test. The influence of the presence of other phases was also analyzed. Refractories showed zircon as the main crystalline phase. In some materials, m-ZrO2 appears coming from zircon dissociation. The thermal shock behavior of refractory of high zircon content is typical of the brittle ceramic materials. Materials showed a relation between elastic module and strength. Dynamic elastic modulus measurements have shown to be suitable for evaluation the TSR for these materials.

CL:P02 Calcium Zirconate as the Secondary Phase of Magnesia Refractories

Jacek Szczerba, AGH - University of Science and Technology, Department of Ceramics, Cracow, Poland

Zirconia and calcium zirconate, despite their relatively high price, are very promising compound of high refractory composites for the steel and cement industry. The Calcium zirconate beside the alumina spinel work especially effectively in magnesia refractories used in sintering zone of rotary kilns in cement industry. The presence of zirconia or calcium zirconate as the components of magnesia and magnesia spinel refractories especially improving the resistance on clinker phase melting and "alkalis attack". The liquid phase in the magnesia product with calcium zirconate phase appears at the temperature of 1555 °C or even higher and it depends on CaO/SiO2 molar ratio. The corrosion resistance researches of magnesia with calcium zirconate to materials (rich of sulphur) from preheater cement kiln were carried out with coating test. The microstructures of the magnesia with the CaZrO3 phase before and after tests were researched by SEM-EDS techniques. The liquid phase formation during the tests is rich of zirconia and calcia. The new phase formation in the materials after tests are clinker phases: β-Ca[SiO4] (C2S), Ca3Al2O6 (C3A) and Ca2AlFeO5 (C4AF but rather as the Ca2Al2O5 (C2A) with Ca2Fe2O5 (C2F)) solid solution and the ternary Ca7Al6ZrO18 (C7A3Z). The sulphur from materials is located in the silicate and aluminate phases.

CL:P03 The Effect of Type of Spinel on the Thermal and Mechanical Properties of Magnesite Refractories

A. Cakir[1, 3]*, S. Turan[2], A. Sesver[3], B. Özdemir[3], [1]Anadolu University, Graduate School of Sciences, Ceramic Engineering Program A.D, Eskisehir, Turkey; [2]AnadoluUniversity, Material Science and Engineering, Eskisehir, Turkey; [3]Kütahya Magnesite Company, Kütahya, Turkey

The replication of temperature variations causes or propagates cracking in refractories. Therefore, knowledge of the thermal and-mechanical properties plays an important role for the safe use of refractories. In this work, fused and sinter spinel were added to magnesite and then density, porosity, cold crush strength, hot strength, thermal expansion, three point bending strength and thermal shock experiments were carried out on the refractories prepared with the addition of different amounts of fused and sinter spinel. Minerological and phase analysis of the representative samples and raw materials were analysed by X-ray diffraction and Scanning Electron Microscope.Mechanical and thermal properties of fused spinel containing refractories were better than sinter spinel containing refractories. Finally, thermal shock tests which selected fused spinel refractories samples were carried out under 500 °C and 1000 °C. The variations of bending strength, elastic modulus and relative strength values were investigated.The mechanical and thermal properties of the refractories containing MgO-fused spinel were found better than the refractories containing MgO-sinter spinel and optimum amount of spinel in the refractories was determined.

CL:P04 Corrosion of an Alumina Refractory by Potassium Salts Refractory in High Temperature Combustion Environments

Na Li*, Leena Hupa, Patrik Yrjas and Mikko Hupa Process Chemistry Centre, Åbo Akademi University, Turku, Finland

The increasing use of biomass and waste derived fuels in combustion challenges the chemical durability of refractories. Durability of an alumina refractory was studied in a chemically aggressive environment. A mixture of potassium chloride and carbonate (molar ratio 1:9) was placed on the sample and heat treated at 700-1000 °C in an electric laboratory furnace in air for one week. Cross-sections of the samples were studied by SEM-EDXA to determine penetration of potassium salts in the refractory. Potassium was found only in the silicate matrix phase of the alumina refractory. Penetration of potassium decreased steeply from the surface to 0.5 mm, after which the decrease was linear and depended on temperature. At 700 and 800 °C the thickness of the matrix layer reacted with potassium was 5 mm, while the layer was thinner at 900 and 1000 °C. At higher temperatures glassy layer consisting of K2O, Na2O, CaO and SiO2 formed on the surface. At 900 °C the thickness of the surface layer was of 10 µm, while the layer was thicker, 200 µm at 1000 °C. The results indicate that potassium salts do react with the refractory. The reactions are complex and strongly dependent on temperature. The importance of these reactions on the practical use of the refractory at these conditions will be discussed.

CM - 2nd International Conference

DISCLOSING MATERIALS AT NANOSCALE

Oral Presentations

Session CM-1
Nanomaterials and Systems at Nanoscale

CM-1:IL02 Synthesis of Nanoparticles of Rare-earth Doped Fluorides

M. Mortier*, P. Gredin, LCMCP-CNRS, Chimie ParisTech and UPMC, Paris, France; G. Patriarche, LPN-CNRS, Marcoussis, France; L. Aigouy, LPEM-CNRS, ESPCI ParisTech, Paris, France

Rare earth doped fluoride nanoparticles such as PbF2, CaF2, compounds in the KF-YF3 phase diagram, have been prepared. The particles have been obtained by different synthesis routes varying from solid state method, such as mechanical allowing by using planetary ball mill, to soft chemistry routes around precipitation processes either in free volume or in nanoreactors obtained in reverse micellar systems. High temperature aqueous syntheses at different temperatures, above 100 °C with precipitation methods or higher 100 °C with hydrothermal systems, have been explored. Also, the chemical attack of nano-composite glass-ceramics allows to get particles. A wide variety of shapes, from spherical to cubic or octahedral, and size distribution, from nanometer to submicron size, has been obtained depending on the growth conditions, the rare earth addition and the crystal phase. These particles have been characterized by mean of X-ray diffraction, Transmission Electron Microscopy and optical spectroscopy. They reveal a strong fluorescence efficiency because of their high crystalline quality and low phonon frequency and also a strong ability to give rise to up conversion energy transfers. Many applications are offered to these particles in the domain of imaging, lighting, thermal measurement...

CM-1:IL03 Nanogaps for Sensing

F. Favier, Institut Charles Gerhardt Montpellier, UMR 5253 CNRS, Université Montpellier 2, Montpellier cedex, France

Modern resistive chemical sensors include discontinuous nano/mesostructures. Sensing performances are then governed by the chemical nature of the nanostructure gap as well as by the sensor design at the nanogap scale. Various top-down, bottom-up and hybrid fabrication routes of discontinuous/nanogaped metal nano and mesostructures have been developed. These structures are assembled/organized on insulating surfaces for integration of resistor based devices for the specific sensing of chemicals in gaseous as well as in liquid media. Hydrogen sensing based on discontinuous/gaped palladium nano/mesostructures is a chosen case-study for the evaluation of various nano/mesogap fabrication methods.

CM-1:IL04 Nanopatterns and Nanomaterials: Synthesis, Characterization and Applications

Hua Zhang, School of Materials Science and Engineering, Nanyang Technological University, Singapore

How to fabricate bio- and nanomaterial arrays in a controlled manner and how to synthesize novel nanomaterials have attracted significant attention because of their importance in a lot of fields including materials, chemistry, biology, sensors, devices, etc. In this talk, I will introduce the researches which have been done in my group recently. These include the dip-pen nanolithography-based controlled fabrication of peptide, Au nanoparticle and CNT arrays on solid substrates, “needle-scratching” method-based fabrication of large-area catalyst patterns used for controlled growth of ultralong (0.5 mm) and high density SWCNTs (10 tubes / µm), synthesis of anisotropic nanomaterials, and graphene derivative-based hybrid materials used for biosensing.

CM-1:IL05 Tailoring Chemomechanical Interface Properties: A Nanomolecular Approach

Ganpati Ramanath, Materials Science and Engineering Department and New York State Center for Future Energy Systems, Rensselaer Polytechnic Institute, Troy, NY, USA

Tailoring interface properties is crucial for diverse applications, e.g., integrated circuits, coatings and composites. I will describe novel strategies to understand and control chemomechanical interface properties using molecular nanolayers (MNLs). Key concepts discussed include nanoglue, nanomechanics of interfacial fracture, and nanoscale reactions at model metal-oxide and metal-polymer interfaces. I will first describe how MNL structure and bonding can influence interface chemical stability and functionality. For example, I will discuss how both hydrophobic and hydrophilic moieties in the MNL can curtail metal diffusion and water uptake. The effects of MNL chemistry and their interplay with nanoscale physical parameters such as interface corrugation and film porosity on interface properties will be revealed via experiments with MNL-treated patterned interfaces and nanoporous materials. Finally, I will demonstrate a nanoglue concept to bind non-sticking materials, and discuss the roles of nanomolecular hooking and ceramization. I will conclude with the first-time experimental quantification of bond-breaking and plasticity contributions to fracture energy by manipulating the MNL bond strength, to pave the way for understanding the nanomechanics of interface fracture.

CM-1:IL06 Morphology-controlled Synthesis of Inorganic Nanostructures

L. Gao, State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China

During the past few years, the rapid arising of nanotechnology has greatly deepened the synthesis chemistry of inorganic nanostructures. Considerable methods have been developed for the synthesis of morphologically special nanocrystals and hierarchical architectures. Meanwhile, the continuous development of the synthetic methods for various nanostructures also motivates to disclose some novel fundamental chemical and physical phenomena. A nanostructure should primarily have the flexibility to tune its geometrical properties, such as the controlled size and/or shape, because these geometrical properties have been demonstrated to affect the physical and chemical performance of the nanostructure dramatically. The present research is focused on the application of some facile and robust synthetic techniques in the preparation of diverse inorganic nanocrystals or microcrystals with controlled morphologies (cube-like, rod-like, hierarchical, etc). Several typical metal oxide and sulfide inorganic nanostructures and hierarchical architectures recently developed by our research group are presented. In particular, the formation mechanisms of these morphologically various architectures are discussed in detail.

CM-1:L07 Processing and Characterization of Multi-Walled Carbon Nanotube - Alumina Ceramic Matrix Composites

Mehdi Estili*, Akira Kawasaki, Department of Materials Processing, Graduate School of Engineering, Tohoku University, Sendai, Japan

Multi-walled carbon nanotubes (MWCNTs) have been dispersed homogeneously within alpha-alumina ceramic with complete interfacial wetting, by combination of our recently established colloidal powder approach and spark plasma sintering. In our powder processing strategy, we successfully addressed the issues of CNT dispersion, interfacial compatibility and mass-production; fully dense ceramic composites containing large amount of MWCNTs can now be fabricated in large amounts. We fabricated nanostructure-controlled functionally graded alumina ceramics employing MWCNTs, by the current processing technology. Microstructural, mechanical and electrical characterization of the composites has been conducted. Structural evolution and mechanical response of MWCNTs in the ceramic environment have been also studied employing nano-manipulation apparatuses equipped with cantilever force sensors. Results show that the MWCNTs become dramatically stronger in the ceramic environment, and thus, are the best candidate to reinforce ceramic-based materials.

CM-1:IL10 Layer-by-Layer Assembly of Transition Metal Oxide Nanosheets Into Functional Ultrathin Films

Takayoshi Sasaki*, Yasuo Ebina, Minoru Osada, International Center for Materials Nanoarchitechtonics(MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan

We have synthesized a variety of transition metal oxide nanosheets, e.g., Ti1-δO2, MnO2, Eu0.56Ta2O7, Cs4W11O36, via delamination of their precursory layered compounds into colloidal single layers, which is triggered by intercalation of quaternary ammonium ions. These nanosheets were found to exhibit enhanced optical, photochemical, electronic, and magnetic properties associated with the molecularly thin two-dimensional structures. We have applied Langmuir-Blodgett technique and sequential adsorption method to deposit these oxide nanosheets layer-by-layer into well-ordered multilayer structures and superlatticel-like films. We have demonstrated that selection of nanosheets and their counterparts as well as precise control over their nanoarchitectures can lead to useful functionalities such as high photocatalytic activities, magneto-optical response to UV light and high dielectric properties at a nanometer scale.

CM-1:IL11 Nanocrystal Based Architectures for Optoelectronics and Photonics

Nikolai Gaponik, Physical Chemistry, TU Dresden, Dresden, Germany

Assembly approaches have been nowadays recognized as main working tool of bottom up chemical nanotechnology. The assembly of strongly emitting semiconductor nanocrystals can be performed on flat, porous and spherical surfaces, thus being important for thin-film technologies, doping of mesoporous materials, modification of pre-patterned substrates, creation of microshells and cavities, etc. Self-assembly approaches or the use of removable templates makes possible the formation of nanowires or nanoporous 3D ordered materials created solely from the assembled nanoparticles. Hierarchical assembling and assembling of nanocrystals with other organic or inorganic entities open up a possibility to achieve architectures with literally unlimited functionalities. The understanding and governing of charge and energy transfer processes between components of assembled composites are the key points in their efficient utilization as building blocks in novel types of LEDs, photovoltaic and photonic devices, as well as various optical sensors.

CM-1:L12 Nano/Micro-protusions on Cu-based Alloys Grown by Ar Ion Irradiation

M. Namatame*, S. Oda, Department of Metallurgy, Tohoku University, Sendai, Japan; S.-I. Tanaka, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

The morphology and growth kinetics of Cu2O nano/micro-protrusions induced by Ar ion irradiation have been extensively studied by the authors' group. In this study, we tried to form protrusions on the Cu-based alloys by Ar ion irradiation and discussed the composition. Irradiated Cu-based alloy was rolled brass plates (Cu 65%- Zn 35%) consisted of alpha(fcc, a=0.370 nm) and beta' (CsCl, a=0.295 nm) phase. Nano/micro-protrusions made of brass having alpha-phase were successfully fabricated on the surface of brass plate by changing Ar ion irradiation conditions. The morphology of irradiated surface changed with Ar ion accelerated voltage: the protrusions grew along grain boundaries or surface flaws having conical shape like flower bud and some grains of the substrate protruded in the case of 5 kV, whereas bundle-like conical protrusions grew on the wavy substrate in the case of 9 kV. The number density of protrusion increased with Ar ion acceleration voltage. The lattice parameter of the protrusions analyzed by glancing angle X-ray diffraction method was larger than that of the substrate material. Composition of the protrusion was also identified using electron probe micro analyzer to discuss its growth kinetics.

CM-1:IL13 Inorganic Nanotubes (INT) and Fullerene-like Structures (IF): Progress Report

R. Tenne, Weizmann Institute of Science, Rehovot, Israel

In this presentation a progress report, focused mainly on the results obtained in our lab will be presented. While the synthesis and study of IF materials and INT from layered metal dichalcogenides, like WS2 and MoS2 remain a major challenge, some progress with the synthesis of IF and INT structures from various other compounds have been realized. Intercalation and doping of these nanostructures, which lends itself to interesting electronic properties, has been realized, too. Recently new core-shell nanotubular structures, like PbI2@WS2 nanotubes have been reported. Major progress has been achieved in elucidating the structure of INT and IF using advanced microscopy techniques, like aberration corrected TEM with 0.08 nm resolution and electron tomography. Also recently, scaling up efforts in "NanoMaterials" resulted in multikilogram production of pure multiwall WS2 nanotubes phases. IF-MS2 (M=W,Mo, etc) were shown to be superior solid lubricant in the form of an additive to various lubricating fluids/greases and for various self-lubricating coating. New potential applications have been realized by forming coatings which incorporate the IF nanoparticles. Some new potential applications for these and related materials will be discussed in the fields high toughness nanocomposites; catalysis; rechargeable batteries. Selective optical coatings which reflect less than 2% of the light over 300-1100 nm will be presented. Such coatings may find numerous applications, among others, in capturing the solar light for thermal energy generation. To capitalize on these opportunities, a production facility for up to 300 kg/day of IF-WS2 in various qualities is being erected and will be in operation in a few months. Large scale sales have started recently.

CM-1:IL14 Rare - Earth - Doped Silicate Glass - Ceramic Thin Films for Integrated Optical Devices

S. Berneschi[1]*, G. Alombert-Goget[2], C. Armellini[2, 3], M. Brenci[1], I. Cacciari[1], A. Chiappini[2], A. Chiasera[2], M. Ferrari[2], S. Guddala[2, 4, 5], E. Moser[4, 2], G. Nunzi Conti[1], S. Pelli[1], G. C. Righini[1], [1]IFAC - CNR, Nello Carrara Institute of Applied Physics, Sesto Fiorentino (FI), Italy; [2]IFN-CNR, Institute of Photonics & Nanotechnology, CSMFO Lab., Povo (TN), Italy; [3]FBK, Trento, Italy; [4]Dipartimento di Fisica, University of Trento, Povo, Italy; [5]School of Physics, University of Hyderabad, Hyderabad, India

The possibility to confine the light in optical planar structures represented the milestone for the development of integrated optical devices in different application areas, such as communications and sensing. In particular, rare-earth (RE) doped planar waveguides demonstrated to be an interesting solution in the realization of integrated optical lasers and amplifiers suitable for the generation/re-generation of the signal in metropolitan and local area networks. Nowadays, although these devices are commercially available, the major contribution of the research consists in discovering and developing better combinations of materials and fabrication processes, in order to reduce the costs and increase the performance of the aforesaid devices. In this context glass-ceramic waveguides, activated by RE ions, seem to fully respond at these requests. The aim of this paper is to offer a comprehensive review on the main results obtained in our Labs in the field of glass-ceramics. Fabrication and characterization of different silicate glass-ceramic thin films, doped with different percentages of RE ions, will be presented and discussed. The interesting results obtained make these systems quite promising materials for development of high performance integrated optical amplifiers and lasers.

CM-1:L16 Er3+/Yb3+/Ce3+ Co-doped Fluoride Glass Ceramics Waveguides for Application in the 1.5µm Telecommunication Window

B.R. Boulard*, I. Savelii, C. Duverger-Arfuso, Y. Gao, LdOF, Université du Maine, Le Mans, France; G. Alombert, Y. Jestin, M. Ferrari, IFN-SCFMO group, Trento, Italy; F. Prudenzano, DIASS, Politecnico di Bari, Bari, Italy

The recent development of transparent glassceramics (TGC) activated by rare earth ions have opened new possibilities in the field of solid state lasers and optical amplifiers, taking benefit of glass properties and crystal-like spectroscopic characteristics. Guided-wave format add several advantages, namely the small size and the larger flexibility in design and fabrication. Since a few decades, fluoride glasses has been identified as a key material for the applications, due to low phonon energy, high solubility of rare earth ions, and flat broad emission at 1.5µm. In this scope, Mortier and al. demonstrated that TGC could be obtained from ZrF4-(La,Er)F3-AlF3 glass (named ZELA) with increased emission cross-section. We will thus present the fabrication by PVD of Ce3+/Yb3+ codoped ZELA planar waveguides, and the ceramisation that produces LaF3 nanocrystals. The pumping at 980nm, not very efficient in single-doped Er3+ waveguides, is increased by the addition of Yb3+ as a sensitizing ion provided Ce3+ is present to avoid up-conversion of Erbium. Structuring of the emission band and effective energy transfer shows that the dopants actually enter the crystal phase and the bandwidth of the emission at 1.5µm (68nm) is much larger that in most Er3+ doped fluoride glass.

CM-1:L17 Nanostructured Titania Films with Improved Photocatalytic Activity

M. Kurtoglu*, T. Longenbach, Y. Gogotsi, Department of Materials Science and Engineering, A.J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, PA, USA

Photocatalytic properties of titanium dioxide (titania) have attracted much attention within the last decade due to titania's photochemical stability and high efficiency. Being a cheap, readily available, and biocompatible material, TiO2 is particularly suitable for use in the large-scale production on light activated films on the surfaces of self-cleaning glassware, air and water purification systems, and self-sterilizing materials. In order to increase the effectiveness of these films, we have explored the effects of dopingnanostructured TiO2 films with various elements that can dissolve in the titania lattice without a significant strain, particularly those which have ionic radiuses similar to that of titanium. A sol-gel process was implemented for the preparation of doped TiO2 films on glass and the experimental results were supported by the density functional theory (DFT). It has been shown that it is possible to significantly increase the photocatalytic activity of TiO2 by carefully selecting the experimental conditions and film composition.

CM-1:L18 **AC-to-DC Power Conversion by As-Grown Single-walled Carbon Nanotube Diodes**

Govind Mallick[1]*, Pulickel M. Ajayan[2], Shashi P. Karna[1], [1]Weapons and Materials Research Directorate, ATTN: RDRL-WM, US Army Research Laboratory, Aberdeen Proving Ground, MD, USA; [2]Department of Chemical Engineering and Mechanical Science, MS-321, Rice University, Houston, TX, USA

Our observation of current rectification property of chemical vapor deposited (CVD), as-grown single-walled carbon nanotube (SWCNT) has led us, for the first time, to investigate the AC-to-DC power conversion through SWCNT transistors. The as-grown long strands of SWCNT bundles are used to fabricate multiple arrays of switching devices with varying channel lengths. A majority of the devices exhibit strong rectification with a forward to reverse current ratio (I(for)/I(rev)) ~10 ^ 5, regardless of the channel length. This unique feature of our as-grown SWCNT devices allowed us to observe AC-to-DC half-wave power conversion in the range of 1-1000 Hz. The power conversion factor remains nearly unchanged over the tested frequency range of 1-200 Hz, but decreases slightly between 200-1000 Hz. The possible reasons of the observed rectification process and underlying mechanism of the observed power conversion factor will be discussed.

CM-1:L20 **Fabrication of Fe-doped SnO2-TiO2 Spinodal Phase-Separated System and Its Semiconductive Properties**

M. Hashimoto*, T. Sekino, S.-I. Tanaka, IMRAM, Tohoku Univ., Sendai, Japan; T. Shimizu, T.Kusunose, ISIR, Osaka Univ., Suita, Japan

Oxide semiconductors SnO2 and TiO2 are originally known as n type semiconductor, and SnO2-TiO2 binary system is known to exhibit an absolute solid solution over 1430 °C and a spinodal decomposition having characteristic lamellar structure. After appropriate annealing, such a phase separation is expected to form a self-organized structure with clear interface between different phases in nanometer scale. In this study, to control various electrical properties of the respective phases, the SnO2 rich phase and the TiO2 rich phase, the trivalent Fe3+ ion is doped to the 0.5SnO2-0.5TiO2 binary solid solution. The 0.5SnO2-0.5TiO2 powder is prepared via solid state reaction from anatase TiO2 and rutile SnO2, whereas the trivalent Fe3+ ion is derived from a-Fe2O3.XRD and SEM analysis revealed that the addition of Fe3+ to SnO2-TiO2 system provided two phases with typical lamellar structure even after the sintering, which might be formed by the similar mechanism to the common spinodal decomposition. Detailed microstructural characteristics and electrical properties such as conductivity, Hall coefficient and so on will be discussed in relation to the materials processing.

CM-1:L21 **Coexistence of Multi-functions in Titanium Oxide Nanotubes Synthesized by a Simple Chemical Route**

Tohru Sekino[1]*, Dong-Jin Park[1], Satoshi Tsukuda[1], Takafumi Kusunose[2], Shun-ichiro Tanaka[1], [1]Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai, Japan; [2]The Institute of Scientific and Industrial Research (ISIR), Osaka University, Ibaraki, Osaka, Japan

Titanium oxide (TiO2) nanotube (TNT) having open-end nano-tubular structure of around 8-10 nm in outer diameter can be synthesized by a low temperature solution chemical method without using any template. Owing to synergetic correlation of low-dimensional structure with physicochemical properties of TiO2, excellent multifunctionality is expected. Recently we found the TNT exhibited both good photocatalytic and molecular adsorption properties in one substance. Adsorption isotherm analysis using methylene blue molecule indicated that the NT followed Langmuir type, and the saturated volume of adsorbate for the as-synthesized NT was fairly large. Further, metal cation doping into NT enhanced the adsorption performance, provably due to the electrostatic effects. Photocatalytic performance increased by heat-treatment and resultant crystallinity increase, while the adsorption property decreased, exhibiting a trade-off relations. Synergy effect of adsorption and photocatalytic properties could also be confirmed for gaseous molecules. Relationships between characteristic low-dimensional nanostructure and the environmental friendly functions and materials modification to enhance the multi-functions will be discussed for the novel nanostructured oxide.

Session CM-2
Nanomaterials Characterisation and Techniques

CM-2:IL01 **Raman Spectroscopy of Functionalized Carbon Nanostructures**

J. Maultzsch, H. Telg*, Institut f. Festkörperphysik, Technische Universität Berlin, Berlin, Germany

Carbon nanotubes and graphene are one- and two-dimensional carbon nanostructures with fascinating physical properties. These properties, such as band-gap energy, vibrational modes, and electron-phonon coupling, depend -besides confinement effects- also on the precise arrangement of the carbon atoms. Raman spectroscopy is particularly suited to probe this relation between atomic structure and physical properties. In this talk we will present experimental results on chemically functionalized carbon nanostructures. Chemical functionalization is important in two different ways: first, it can be required to functionalize nanostructures in order to provide a specific sample environment, e.g. aqueous solution, and second, functionalization may aim at tuning the physical properties in a controllable way. Therefore, we will discuss the effect of several types of functionalization on the vibrational properties, optical transition energies, and electron-phonon interaction in carbon nanostructures.

CM-2:IL02 **Non-contact Atomic Force Microscopy for Nano-characterization**

Masayuki Abe*, Yoshiaki Sugimoto, Seizo Morita, Graduate School of Engineering, Osaka University, Suita, Japan

Scanning probe microscopy (SPM) enable us to investigate surface structure and properties in nano level. As an SPM method, non-contact atomic force microscopy (NC-AFM) has an atomic resolution. In this lecture, we would like to talk about our recent results of NC-AFM at room temperature (RT). In a RT condition, AFM tip-sample position change due to thermal drift had disturbed precise and reproducible measurements. We had succeeded in compensating the thermal drift with the atom-tracking and feedforward (AT&FF) technique[1, 2], which enabled us to tip-sample positioning at 10pm-precision at even RT. This enabled us to perform application measurements such as site-specific force spectroscopy to identify surface atom species[3]. And the AT&FF can be used for atom manipulation experiments at RT condition for structuring atomic pattern[4]. These results of the atom identification and the atom manipulation should be key roles for the nano-characterization.

[1]M. Abe et al, Appl. Phys. Lett. vol. 87, p. 173503 (2005); [2]M. Abe et al, Appl. Phys. Lett. vol. 90, p. 203103 (2007); [3]Y. Sugimoto et al, Nature vol. 446, p. 64 (2007); [4]Y. Sugimoto et al, Science vol. 322, p. 413 (2008)

CM-2:IL03 **Size and Surface Effects on Emission Properties of Lanthanide Doped Upconversion NaYF4 Nanoparticles**

G.M. Chow, Department of Materials Science and Engineering, National University of Singapore, Kent Ridge, Republic of Singapore

NIR-to-visible upconversion (UC) nanoparticles have potential applications for bio-probes and solar cell enhancement. Most work on UC nanoparticles has been focused on NaYF4:Yb,Er. The emission intensity of these UC nanoparticles is significantly reduced compared to their bulk counterparts. In this talk, an overview of our recent work on NaYF4 nanoparticles is presented[1-4]. NaYF4:Yb,Er/NaYF4/polymer (core/shell/shell) nanoparticles showed enhanced UC fluorescence. The emission intensity of NaYF4:Yb,Er/NaYF4/silica (core/shell/shell) nanoparticles increased by 15 times compared to that without the intermediate undoped NaYF4 shell. The critical shell thickness of undoped NaYF4, prevention of non-radiative transfer and undesirable dopant surface segregation were studied.

[1]G.S. Yi and G.M. Chow, Advanced Functional Materials, 16:2324 (2006); [2]G.S. Yi and G.M. Chow, Chemistry of Materials, 19:341 (2007); [3]D. Yuan, G.S. Yi and G.M. Chow, Journal of Materials Research, 24:2042 (2009); [4]L.P. Qian, D. Yuan, G.S. Yi and G.M. Chow, Journal of Materials Research, in press.

CM-2:IL04 **Low-frequency Raman Scattering in Nanometric Structures**

A. Mermet*, E. Duval, L.P.C.M.L., Université Lyon 1, Villeurbanne Cedex, France

In the GHz-THz spectral range, two types of inelastic low-frequency light scatterings by vibration modes in solids can be observed: Brillouin scattering by acoustic propagating modes, and Raman scattering by modes that are localized or quasi-localized over nanometric distances. Localization (or quasi-localization) in solids can be induced by structural disorder like in amorphous or glassy materials. It is clear-cut in nanoparticles like nanocrystals embedded in solids or self-assembled in a super-organization. Vibration localization in biological nano-objects such as viruses may be also studied. In the first part of the talk, eigenmodes of a spherical nanoparticle will be described, together with their activity for Raman scattering. The effects of nanocrystals' crystallinity will be considered. Several examples of Raman scattering by metallic and insulating dielectric nanocrystals will be given as an illustration. In the second part of the talk, the case of glasses will be discussed. We will show how, from the point of view of Raman scattering, the comparison with nanoparticle assemblies points to the hybridization of quasilocalized modes from nanometric domains with propagating acoustic modes.

CM-2:IL05 **STEM Characterization of Atomic Structures and Segregated atoms at Ceramic Interface**

Y. Ikuhara[1, 2, 3]*, Y. Sato[1, 2], N. Shibata[1], T. Mizoguchi[1], T. Yamamoto[1, 2], [1]Institute of Engineering Innovation, The University of Tokyo, Tokyo, Japan; [2]Nanostructures Research Laboratory, Japan Fine Ceramic Center, Nagoya, Japan; [3]WPI Advanced Institute for Materials Research, Tohoku University, Sendai, Japan

Grain boundaries and interfaces of crystals have peculiar electronic structures, caused by the disorder in periodicity, providing the functional properties, which cannot be observed in a perfect crystal. In the vicinity of the grain boundaries and interfaces around the order of 1 nanometer, dopants or impurities are often segregated, and they play a crucial role in the material properties. We call these dopants "function providing elements", which have the characteristics to change the macroscopic properties of the materials drastically. In this presentation, the results obtained by Cs (spherical aberration) corrected STEM are demonstrated for well-defined grain boundaries in Al_2O_3 and ZnO bicrystals doped with Y and Pr. In addition, several examples are also demonstrated to characterize the interface structures of $SrTiO_3$ superlattice, $LiFePO_4$ and Au/TiO_2 catalytic system by Cs corrected STEM.

CM-2:IL06 **Effects of Surface Hydrogenation on Diamond-like Carbon Films by In-situ UPS**

Daniel H.C. Chua, Department of Materials Science & Engineering, National University of Singapore, Singapore

The characteristics of surface hydrogenation on crystalline diamond films have been well known. In this lecture, we present the physical effects of surface hydrogenation on diamond-like carbon films, focusing on ta-C, by in-situ UPS/XPS. We show that surface hydrogenation does impart unique surface properties to the material with little or no effects on the bulk properties. Microwave plasma CVD is first used to modify the surface of ta-C films. The formation of C-H bonds on the surface is confirmed by HREELS and in-situ UPS/XPS further shows a reduction in the work function by ~1eV. The hydrogen terminated surface is stable up to 600 °C after which hydrogen desorbs from the surface. We further report that the hydrogen terminated surface leads to a lowering of the turn-on field, where a low 7V/um for electron field emission was shown while both pristine and >600 °C annealed films emit at >20V/um. AFM studies show that the annealing does minimal changes to the surface morphology. From these findings, we are able to engineer electron emitter tips and excellent electron emission are obtained when vertically aligned 1-D structures are combined with thin surface hydrogenated ta-C films, forming a core-shell structure. The physical properties of the hybrid structure will be discussed.

CM-2:L07 **MgO Nanocubes in Compressed Powders**

A.K. Sternig, D. Koller, N. Siedl, M. Müller, J. Bernardi, O. Diwald*, Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria; Institute of Particle Technology, Friedrich-Alexander-University, Erlangen, Germany; K.P. McKenna, P.V. Sushko, Alexander L. Shluger, London Centre for Nanotechnology and Department of Physics & Astronomy, University College London, London, UK; WPI-Advanced Institute for Materials Research, Tohoku University, Sendai, Japan

Optical and charge trapping properties of oxide nanoparticle ensembles are strongly affected by the presence of interfaces between particles[1]. For this combined experimental and theoretical study we used MgO nanocubes with adjustable size distributions as a model system[2] to explore the complex electronic properties of particle interfaces and grain boundaries. Interaction-induced changes in the electronic surface properties were experimentally investigated on a series of MgO nanocube powders, which - prior to the spectroscopic measurement - had been subjected to external pressures. After vacuum annealing of the compressed powders we quantitatively characterized optical properties in terms of absorption and photoluminescence in the UV/Vis region. Potential changes in nature and yield of trapped charges were investigated by electron paramagnetic resonance spectroscopy. The spectroscopic results were related to particle coarsening and sintering effects that were tracked by XRD and electron microscopy measurements and discussed in the light of results from first-principles calculations.

[1]McKenna K.P., Sushko P.V., Shluger A.; J. Am. Chem. Soc. 129 (2007) 8600; [2]Stankic S., Muller M., Diwald O., Sterrer M., Knozinger E., Bernardi J., Angew. Chem. Int. Ed. 44 (2005) 4917

CM-2:L08 **Scanning Auger Electron Spectroscopy: a New and Universal Technique for Identifying Graphene**

Mingsheng Xu*, International Center for Young Scientists, National Institute for Materials Science, Japan; Daisuke Fujita, International Center for Young Scientists, Advanced Nano Characterization Center, International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Japan; Nobutaka Hanagata, Nanotechnology Innovation Center, National Institute for Materials, Japan

Graphene, a single sheet of sp2-bonded carbon arranged in a honeycomb lattice, has unusual electronic, optic properties, and exhibits single-molecule sensitivity to the change of conductivity. These superb characteristics of graphene open new possibilities of applications in electronic devices, such as high-speed and radio frequency logic devices and solar cells, and sensors to detect single-molecule events. Currently, Laser Raman spectroscopy is used as a standard technique to identify monolayer, bilayer, and few-layer graphene. It may evaluate the quality of graphene films indicated by presence of the D peak and shift of the intense peaks. However, Raman spectroscopy of graphene films is strongly dependent on the substrate, on which the graphene films are, and individual instrument used for the characterization. Both the factors significantly influence intensity and positions of the features. Auger electron spectroscopy (AES) is a surface sensitive technique and is usually used for ultrathin film analysis. Here we report for the first time AES as a universal technique for identification of layers and composition of graphene films at the nanoscale levels.

This work was partially supported by the budget for commission of MEXT; and the WPI Initiative on Materials Nano-architectonics, MEXT, Japan

CM-2:L09 **Synthesis of Carbon Nanotubes/Gold Nanoparticles Hybrids for Environmental Applications**

L. Minati[1]*, G. Speranza[1], S. Torrengo[1, 2], L. Toniutti[2], B. Rossi[2], C. Migliaresi[3], D. Maniglio[3], A. Chiasera[4], M. Ferrari[4], [1]FBK, Povo-Trento, Italy; [2]Dept. Physics, University of Trento, Italy; [3]Dept. Material Eng., University of Trento, Italy; [4]CNR-IFN, CSMFO Lab., Povo-Trento, Italy

Carbon nanotubes/nanoparticles hybrid materials in this last decade have received much attention by the scientific community due to their potential applications. In particular, the synergetic effect between the properties of the elements which constitute a single nanostructure has triggered intensive studies. In this work we show how carbon nanotubes functionalized with biomolecules and metal nanoparticles open the possibility to produce efficient biomarkers. Multi-walled carbon nanotubes were chemically cut by acid treatments and then functionalized with short thiol chains (2-aminoethanethiol). Gold nanoparticles were then bonded to the nanotubes to exploit their plasmon resonances. Reaction intermediate as well as the final products were analyzed by X-Ray Photoelectron Spectroscopy, Infra-Red Spectroscopy, Scanning Electron Microscopy and Atomic Force Microscopy. Since carbon nanotubes efficiently support the gold nanoparticles an efficient Raman enhancement of toxic anions is obtained. This is of particular interest for the detection of substances dangerous for the environment and human health.

CM-2:L10 **New MoO3-x Nanowire Based Materials for Polymer-fiber Composites**

V. Domenici[1]*, M. Conradi[2], M. Remskar[3], A. Mrzel[3], M. Chambers[4], B. Zalar[3], [1]Dipartimento di Chimica e Chimica Industriale, Università degli studi di Pisa, Pisa, Italy; [2]Institute of Metals and Technology, Ljubljana, Slovenia; [3]J. Stefan Institute, Ljubljana, Slovenia; [4]Krsko Nuclear Power Plant, Krsko, Slovenia

Low dimensional materials often show exceptional properties compared to those of the corresponding macroscopic compounds, especially beyond the linear regime of the force-deformation curve. The MoO3-x nanowires belong to photocromic materials and are promissing candidates for lithium intercalation, hydrogen sensing and smart windows. Currently, a development of nanomaterials promotes in a direction of multi-functional polymer composite structures, which prevent releas of nanoparticles into atmosphere and eliminates a possible health effects of nanowires. We report on a successful preparation of liquid single crystal elastomers (LSCE) containing MoO3-x nanowires, mostly the conductive Mo5O14 phase. This particular combination of molybdenum based nanowires and LSCE enables functionalization of single-crystal elastomers preventing the pristine mechanical and optical properties of the host matrix. Polarized optical microscopy has been used for revealing a tendency of nanowire orientation along the director of the LSCE, while the surface topography was studied with atomic force microscopy in a tapping mode. Conductive measurements on the new composite materials in the form of thin films will be also discussed.

CM-2:L11 **Structure Analysis of Nanocomposite Materials for Energy Related Applications**

Michel L. Trudeau*, Alessandra M. Serventi, Karim Zaghib, Materials Science, Hydro-Quebec Research Institute, Varennes, Quebec, Canada; David Antonelli, Sustainable Energy Research Center, University of Glamorgan, Pontypridd, UK; Raynald Gauvin, Department of Mining and Materials Engineering, McGill University, Montréal, Québec, Canada

The enhanced industrial applications of new nanostructured materials, as well as the need to understand the behaviour, as well as the degradation processes, of older materials with nanometer structures, necessitate an increased use of HRTEM for structural and, even more, for analytical analysis at the sub-nanometer level. This is even truer for the field of energy research today. For this reason, the Hydro-Quebec Research Institute has acquired a Hitachi HD2700C dedicated STEM with a CEOS aberration corrector and a cold field emission gun, equipped with a specially designed EELS Spectrometer from Gatan and a newly designed SDD EDS detector from Bruker. This dedicated STEM has demonstrated an image resolution of 78 pm in HAADF and an information resolution of the order of 50 pm in BF. Moreover, this unique combination of a cold emitter, a CEOS corrector and this new SDD detector allows for very fast EDS elemental analysis with the real possibility of elemental mapping at the nanometer or even sub-nanometer level. In this work, we will show the strategic importance of this high resolution tool for a variety of energy related research fields, from new carbon nanotube nanocomposites that are being developed for electrical components, to new electrodes for Li-ion batteries and to the better understanding of more conventional materials such as Zr2.5Nb pressure tube alloy used in nuclear reactors, for which some mechanical properties seem to correlate to the grain structures and composition at the nanometer level.

CM-2:L13 **XPS Study of In Situ One-Step Ammination of Nanocrystalline Diamond Films**

S. Torrengo[1, 2]*, A. Miotello[1], G. Speranza[2], L. Minati[2], M. Ferrari[3], A. Chiasera[3], M. Dipalo[4], E. Kohn[4], 1Physics Dep. University of Trento, Povo, Trento, Italy; [2]FBK-IRST, Povo, Trento, Italy; [3]CNR-IFN, CSMFO Lab., Povo, Trento, Italy; [4]Institute of Electron Devices & Circuits, Ulm University Ulm, Germany

The recent advancement in coupling the semiconductor technology with biological molecules has given the possibility to develop biosensors for specific purposes. The hydrogenated diamond surface is one of the best platforms to develop a biosensor since it possesses rather unique properties. Among the other, diamond is highly chemically inert and then highly biocompatible. Grafting of biomolecules is highly stable in air and in aqueous environments. Finally the hydrogenated diamond surface is conductive while oxidized diamond is resistive. All these properties are the required ingredient to fabricate a surface gate field effect transistor (SGFET) for an organic label free molecular recognition. The diamond surface conductivity is very sensitive to the molecular species on its surface. Diamond based SGFET may then be used to detect the DNA hybridization. On the other hand, DNA recognition requires DNA single strands to be bonded to the FET active zone. At this aim, ammination of the diamond surface is needed. In this work we report a XPS in situ study of direct nano-crystalline diamond ammination using ammonia gas in order to understand the chemical reaction that happens on the diamond surface.

CM-2:L14 **Manufacturing of Barium Titanate Thin Films with Designed Microstructure by a Sol-gel Process: In-situ SAXS Investigation of the Precursor System**

T.M. Stawski*, S.A. Veldhuis, J.E. ten Elshof, H.L. Castricum, D.H.A. Blank, University of Twente, Inorganic Materials Science Group, Enschede, The Netherlands

Barium titanate (BTO) is used as a high-k dielectric material in multi-layer ceramic capacitors. The minimum BTO layer thickness that can be achieved commercially with the state of the art tape casting methods is about 0.5 µm, which implies the use of starting powders with a particle size of ca. 100 nm. Further downsizing requires finer powders. Wet-chemical methods based on sol-gel reactions are among most thoroughly investigated, and can also be applied to make BTO. Knowledge of the size, shape and kinetics of primary sol-gel derived oligomeric nanostructures in solution is crucial to optimize the processing of functional oxide thin films from these solutions. The barium titanate sol-gel precursor system was analyzed by small angle X-ray scattering analysis at the DUBBLE beamline at the ESRF in Grenoble. BTO sols were formed in the reaction of barium acetate, titanium isopropoxide and water in glacial acetic acid and 2-methoxyethanol. The relationship between size and dimensionality of the oligomers, and the influence of synthesis conditions (temperature, concentrations of reactants) were investigated. Evolutionary, systematic changes in the radii of gyration (Rg) and internal structure of colloidal sols (characterized by the fractal dimension, Df) were monitored as a function of time.

Session CM-3
Nanomanufacturing

CM-3:IL02 **Opal-type Photonic Crystals: Fabrication and Application**

Andrea Chiappini[1]*, Guillaume Alombert-Goget[1], Cristina Armellini[1, 2], Simone Berneschi[3], Massimo Brenci[3], Ilaria Cacciari[3], Claire Duverger-Arfuso[4], Sriram Guddala[1, 5, 6], Maurizio Ferrari[1], Enrico Moser[1, 5], D. Narayana Rao[6], Giancarlo C. Righini[3], [1]CNR-IFN, CSMFO Lab., Povo, Trento, Italy; [2]FBK, Povo, Trento, Italy; [3]CNR-IFAC, Nello Carrara Institute of Applied Physics, MDF-Lab, Sesto Fiorentino (FI), Italy; [4]Lab. LdOF, UMR CNRS 6010, Université du Maine, Le Mans, France; [5]Dipartimento di Fisica, Università di Trento, Povo, Italy; [6]School of Physics, University of Hyderabad, Hyderabad, India

Photonic crystals (PhCs), artificially created periodic structures of dielectric materials, hold promise for innovative light manipulation structures which can be viewed as a subclass of a larger family of metamaterials. A simple and inexpensive method to realize PhCs in opal configuration exploits the properties of self-assembly of colloidal nano- and micro-spheres. These spheres and the derived self-assembled structures can be doped with different kinds of cromophores and can also be coated by noble metals. In this sense, applications to active metamaterials and plasmonics-based devices, suitable as fluorescent markers, as well as for luminescence enhancement, are possible. In this lecture we will focus the attention on the different techniques developed for the formation of opals structures. Moreover, starting from these structures, different colloidal crystals are developed. In particular we'll discuss the results obtained on silica inverse opals activated by Er3+ ions. Finally, it will be shown as opal infiltrated with suitable elastomeric polymers can be used as strain sensors, and we'll discuss the properties of metallodielettric colloidal structures that can be suitable as chemical or biological sensors.

CM-3:IL03 **Self-assembly and Soft Lithography for Nanostructure Fabrication**

Heiko Wolf*, Cyrill Kümin, Emanuel Lörtscher, Antje Rey, IBM Research GmbH, Zurich Research Laboratory, Rüschlikon, Switzerland; Cathrein Hückstädt, Nicholas D. Spencer, Department of Materials, ETH Zürich, Zürich, Switzerland

The special properties of nanoscale objects, such as metal and semiconductor nanoparticles, nanowires, or nanotubes, make them promising building blocks of novel optical and electronic devices. The systematic fabrication of devices usually requires the integration of these heterogeneous materials into a larger, ordered structure. More complex device architectures may, in addition, entail the selective assembly of several different types of small objects into pre-defined locations or demand an assembly with the correct orientation when such objects are non-spherical. Here, we describe a technique that uses a combination of templated self-assembly and printing with elastomeric stamps to fabricate defined particle arrays with high yield and accuracy. The assembly step is performed from an aqueous colloidal suspension onto a patterned template. The template is a silicone elastomer replica of a 3D-structured silicon master. During an adhesive transfer step, the assembled particles are printed onto the target substrate. Strategies for a size-selective assembly process and for control of orientation during the assembly of gold nanorods will be discussed.

CM-3:IL04 Iron Oxide Nanostructural Materials and Their Enhanced Sensing Performance

D. Wang*, IPE CAS, Beijing, China; R.B. Yu, USTB, Beijing, China; X.Y. Lai, J. Li, Z.M. Li, IPE CAS, Beijing, China

Iron oxides are among the most important magnetic materials and have been widely used in electronic devices, information storage, magnetic resonance imaging (MRI), and drug-delivery technology. Nanostructural materials often exhibit special physical and chemical properties different from bulk materials, owing to their larger specific surface area, and special structure. According to these properties, iron nanostructural materials are expected to have advantages over their bulk material counterparts in some areas including catalysis, adsorbents and gas sensors. Herein, we report some general methods applicable to synthesis of nanostructure material, hollow microspheres of iron oxides by using hard template method and hydrothermal self-assembly method. The products were characterized by X-ray powder diffraction, scanning electronic microscopy, transmission electron microscopy and nitrogen sorption measurement. The effects of the synthesis conditions have been studied. The size and shell structures of hollow spheres obtained can be manipulated by changing the synthesis conditions. Gas-sensor investigations revealed the iron oxides hollow spheres used as gas-sensor materials possess high sensitivity and quick responses to organic gases.

CM-3:IL05 SPM-based Nanofabrication and Analysis of Atomic-scale Magnetic Systems

Roland Wiesendanger, Interdisciplinary Nanoscience Center Hamburg, University of Hamburg, Hamburg, Germany

Advances in the emerging field of Nano-Spintronics depend critically on a fundamental understanding of magnetic properties and interactions at the atomic level. The direct visualization of atomic-scale spin structures has first been accomplished by combining the atomic resolution capability of Scanning Tunnelling Microscopy (STM) with spin sensitivity. The resulting technique, Spin-Polarized STM (SP-STM), nowadays provides unprecedented insight into collinear and non-collinear spin structures at surfaces of magnetic nanostructures and has already led to the discovery of new types of magnetic order at the nanoscale. More recently, the development of sub-Kelvin SP-STM has allowed studies of ground-state magnetic properties of individual magnetic adatoms on non-magnetic substrates as well as the magnetic interactions between them. By combining SP-STM with single-atom manipulation techniques, prototype nanoscale spintronic devices now become experimentally accessible. Moreover, the combination of spin state read-out and spin state manipulation, based on spin-current induced magnetization switching across a vacuum gap by means of SP-STM, provides a fascinating novel type of approach towards ultra-high density magnetic recording without the use of magnetic stray fields.

CM-3:IL06 Supramolecular Approaches for Novel Functional Hybrid Materials

Katsuhiko Ariga, World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan

Design, synthesis, and fabrication of organic/inorganic hybrids with nano-sized structural features can be done based on appropriate supramolecular approaches from unit molecular structures. Various nanoscopic and microscopic morphologies were successfully constructed through self-assembling and designed-assembling process. For example, a novel hierarchic nanostructure based on layer-by-layer (LbL) assembly and mesoporous technology, so-called “mesoporous nanocompartment film”, was reported. The nano-compartment films exhibit stimuli-free auto-modulated material release, unlike previous examples, due to the special morphology of silica capsules. LbL films of mesoporous carbons were developed for sensors based on highly cooperative adsorption of guests into nanopores. As the other examples, designed assemblies of ultra-narrow-size PbS nanorods and gold nanoparticles have been also fabricated. Especially, the former nanorods can be hybridized with liquid crystalline materials for electrically-driven display applications. Structure transcription of molecular assembly resulted in well-structured bulk materials such as novel nanocarbon materials “carbon nanocage”, which exhibited unique material separation properties.

CM-3:IL07 Luminescent Nanoparticles as Efficient Labels in DNA-Microarray

F. Enrichi*, R. Ricco’, A. Meneghello, CIVEN and Nanofab, Marghera (Venezia), Italy

DNA microarray is a high-throughput technology that consists of an arrayed series of spots of ssDNA, called probes, each containing a specific nucleotide sequence. Probe molecules can hybridize a target sample and this event can be identified and quantified by means of optical, fluorescence-based detection. To improve the sensitivity of the microarray and to avoid limitations related to common dyes (photobleaching, low chemical stability, etc.) the development of new and better biolabels is desiderable. In this talk the work done at Civen/ Nanofab about the synthesis and characterization of luminescent silica spheres doped either by rare-earth ions or by organic dyes is presented. Their application in DNA microarray technology in comparison to the use of standard fluorophores or commercial quantum dots is discussed, demonstrating their better efficiency with respect to other approaches. Moreover silica nanospheres have many advantages because they can be uniform, well controlled in size, stable in water, highly luminescent, non toxic and easily functionalized. All these aspects make them very promising for present and future applications in bio-labeling and bio-imaging.

CM-3:IL08 Design of Size and Interconnection of Novel Complex Oxide Powder

Satoshi Wada, University of Yamanashi, Kofu, Japan

To enhance physical properties, it is known well that polarization rotation mechanism is very important for dielectric and piezoelectric materials. To apply the polarization rotation mechanism for property enhancement, a new material design using different complex oxide nanocubes was proposed. In this study, a novel complex oxide accumulation of barium titanate (BaTiO3, BT) and strontium titanate (SrTiO3, ST) nanocubes was prepared. For this objective, a concept of molecular recognition was applied in this study. As a result, using DNA base pair such as adenine and thymine, 3-dimentional artificial superlattice accumulations were prepared without any external fields, and checkerboard-like structure composed of BT and ST nanocubes was successfully prepared with a size of around 100 nm. However, this size is too small to measure dielectric property. Thus, some external fields such as electric and magnetic-fields were applied during self organization of BT and ST nanocubes, and thus, their sizes became over 10 mm. Their dielectric property will be reported at the presentation.

Session CM-4
Theory, Modeling and Simulation

CM-4:IL01 Simulation of Complex Photonic Materials

A. Quandt*, A. Leymann, Institut fuer Physik, Universitaet Greifswald, Greifswald, Germany

Many technologically interesting applications of photonic (meta-)materials require a certain fine-tuning of their basic dielectric matrix, and therefore it might be necessary to combine experimental approaches with reliable numerical simulations. We report about a recent initiative to supply some suitable domestic simulation tools from scratch, in a form where those methods could easily be run and modified by anybody with just a basic knowledge of programming. To this end we implemented the popular frequency domain methods into various numerical packages like MAPLE and MATLAB, and determined the photonic band structures of a series of complex dielectrics. We will briefly review the main components of such a photonic band structure program, and describe our attempts to accelerate the basic numerical procedures, in order to be able to treat rather complex dielectric materials in the most efficient manner. We will also demonstrate how to apply our code to determine, analyze and visualize the band structure of various periodic, aperiodic and quasiperiodic photonic crystals. A special focus will be on a complete survey of gap maps for Archimedean tilings. Finally we will discuss future improvements and modifications.

CM-4:IL02 Finite Bias Effects on the STM Images and STS Spectra of C60 Weakly Coupled to Au(111)

M. Cobian, F.D. Novaes*, A. Garcia ICMAB-CSIC, Campus de la UAB, Bellaterra, Spain; H. Ueba, Department of Electronics, Toyama University, Gofuku, Toyama, Japan; P. Ordejon, N. Lorente, CIN2, Campus de la UAB, Bellaterra, Spain

Molecular entities at the interface with an inorganic surface are the basis for new hybrid functional materials for microelectronics. In most cases, strong bonding of molecules to metal surfaces perturbs the discrete molecular energy levels leading to a broadening of the molecular density of states. Deposition of C60 on a Au(111) surface previosly exposed to tetraphenyl adamantane give rises to a nanostructured organic layer where the electronic coupling between the C60 and the Au(111) surface is significantly reduced compared to C60 on a clean Au(111) surface[1]. In this case the molecular states of C60 remain more localized and less broadened, thus giving rise to strong non-linearities in the electron transport through the organic-inorganic interface. Calculations based on Density Functional Theory reveal that intermolecular interactions lock C60 into a particular orientation. Scanning tunneling spectroscopy experiments on such system exhibit the presence of negative differential resistance that motivated the simulation of the transport properties at ab-initio level using TRANSIESTA.

[1] KJ. Franke, G. Schulze, N. Henningsen, I. Fernandez-Torrente, JI. Pascual, S. Zrwell, K. Ruck-Braun, M. Cobian, N. Lorente, Physical Review Letters 2008, 100, 036807

CM-4:IL03 Multiscale Simulation of Nanostructured Photovoltaic Cells

Zhigang Shuai, Dept. of Chemistry, Tsinghua University, Beijing, China

Highly efficient photo-induced charge transfer in blend polymer promises huge potential application in organic solar cells. We have established a model for blend polymer with electron donating and accepting composites. The nanostructure formed by the two components is simulated by Ising model. The first reaction method (FRM) is successfully applied to describe the key microscopic processes, including exciton generation, diffusion, dissociation at the nano-interface, and the diffusion, as well as the charge collection by the electrodes, through a dynamical Monte Carlo simulation.

CM-4:IL04 Lithography Simulation: Modeling and Applications

Peter Evanschitzky*, Andreas Erdmann, Fraunhofer IISB, Erlangen, Germany

Today, optical lithography at 193 nm is used to achieve a minimum feature size of 45 nm for the patterning of microelectronic circuits. The continuous decrease of feature dimensions with sizes considerably smaller than the wavelength of the used light results in a tremendous increase of the complexity of lithographic processes. Modeling and simulation of lithographic processes have become mandatory for the development and optimization of new processes. This article reviews standard and advanced modeling techniques in lithography simulation. Rigorous electromagnetic field solvers in combination with vector imaging models predict the image formation inside the photoresist. Semi-empirical macroscopic and microscopic models describe physical and chemical phenomena during the processing of resists. Various optimization techniques are applied to identify the best exposure and process parameters. Several examples like source/mask optimization, different options for double exposure and double patterning, and mask induced imaging artifacts in EUV lithography demonstrate the application of predictive simulations. Furthermore, the application of lithography simulation for the modeling of alternative exposure techniques for special micro- and nanotechnology applications is illustrated

CM-4:IL05 Computational Modeling and Design of Point Defects in Bioactive Calcium Phosphates

K. Matsunaga, Department of Materials Science & Engineering, Kyoto University, Kyoto, Japan; Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, Japan

Hydroxyapatite (HAp) is one of bioactive calcium phosphates, and is expected to further improve its good bioactivity and biocompatibility for practical application to bone replacement. However, chemistry of HAp is rather complicated, because HAp components in bone and tooth contain various kinds of point defects and impurities, which are closely related to the biological properties. It is thus important to reveal atomic and electronic structures, and energetics of point defects involved in HAp. In this study, first-principles calculations of point defects in hydroxyapatite and apatite-related calcium phosphates were performed, and defect formation energies were evaluated from first-principles total energies and ionic chemical potentials. Chemical equilibrium between HAp and aqueous HAp-saturated solutions was assumed, and solution-pH dependence on defect formation energies was investigated. Stable defect structures inducing Ca deficiency of HAp, ionic substitutions via ion exchange mechanism, and interactions between Ca vacancies and dopants (or impurities) will be discussed.

CM-4:IL06 1D Nanostructures from Carbon and Other Elements

G. Seifert, Physikalische Chemie, Technische Universität Dresden, Dresden, Germany

One-dimensional (1-D) nanostructures, such as nanorods, nanotubes, nanowires, nanoribbons and nanobelts, have been of both fundamental and technological interest during the past two decades due to the interesting electronic and physical properties intrinsically associated with their low dimensionality and quantum confinement effect. For instance, graphene nanoribbons, thin strips of graphene or unrolled single-walled carbon nanotubes with nanometer-sized width, have been successfully synthesized recently. 1-D nanomaterials hold extremely promising applications in the future nanoscale electronic devices, as one only one example for applications. Such nanostructures are not limited to carbon. Inorganic fullerenes, nanotubes, nanowires and “inorganic graphenes” may have exceptional properties and bring new breakthroughs in nanomaterials science. However, this field is currently overshadowed by carbon based structures. The intrinsic properties and the potential for new nanomaterials with interesting physical and chemical properties of such inorganic systems, will be discussed in comparison with the corresponding carbon systems. Especially, the electronic, magnetic and mechanical properties of such structures will be discussed on the basis of theoretical investigations.

CM-4:L07 Theory of Molecular Electronics: Wires, Diodes, and Transistors

Shashi P. Karna*, Govind Mallick, US Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD, USA; Haying He, Ravindra Pandey, Department of Physics and Multi-Scale Technology Institute, Michigan Technological University, Houghton, MI, USA

Organic molecular electronics has attracted a great deal of attention in recent years due to a continued miniaturization of current solid-state microelectronics and the emergence of nano-scale devices using exotic new materials, such as nanotubes, nanosheets, and semiconductor quantum dots. Organic molecules, in addition to offering versatility of structural modification, ease in synthesis, and potentially low cost of production, also offer a unique advantage - control of electron transport by geometry and electronic structure modification - that other materials do not offer. In the recent years, we have investigated the effects of length, functional substituent, electronic structure, and geometry on the current-voltage characteristics of organic molecular systems by first-principles quantum chemical methods. This paper will present the results of our recent studies on organic molecular wires, diodes, and transistors to understand and establish fundamental mechanisms of electron transport and to develop functional device concepts.

CM-4:L08 Thermal Conductivity of Ceramic Nanocomposites - The Phase Mixture Modeling Approach

Willi Pabst*, Jan Hostasa, ICT Prague, Institute of Chemical Technology, Prague, Dept. Glass and Ceramics, Prague, Czech Republic

In nanocrystalline materials the grain boundaries must be considered as regions of finite thickness with properties different from the crystalline bulk material present in the crystallite cores. Thus, dense (i.e. pore-free) single-phase nanocrystalline materials can be considered as quasi-two-phase systems whose effective properties can be calculated when quantitative thickness information is available and the property value of the grain boundary phase can be reliably estimated. Similarly, dense two-phase nanocomposites may be considered as quasi-three-phase systems and their effective properties can be predicted using an analogous phase mixture modeling approach. In this contribution this is done for the thermal conductivity of alumina-zirconia nanocomposites. In particular, a two-stage homogenization procedure is applied, consisting of a first step, in which the alumina-zirconia composite is treated as a symmetric-cell material, and a second step, in which the highly disordered grain boundary phase is treated as a matrix-phase coating the crystallite cores. The individual averaging steps are discussed with respect to the two- and three-point bounds, and the resulting grain size dependence is compared with that of pure nanocrystalline alumina and zirconia, and literature data.

CM-4:L09 Estimation Technique for Optical Dielectric Constant of Polymorphous SiO2 Through First-principles Molecular Orbital Calculation

K. Hirose*, D. Kobayashi, Institute of Space and Astronautical Science, JAXA, Japan; S. Igarashi, H. Nohira, Tokyo City University, Japan

It is extremely valuable to be able to compute the dielectric properties of materials used in advanced nanodevices. First-principles calculations have provided several types of approaches for estimating the optical dielectric constant e of materials. They also give useful physical insights into the parameters contributing to e that cannot be clarified by any other means. Recently we have proposed a new technique for estimating e for Si and Al compounds through the first-principles molecular orbital calculation of the Slater transition state which we developed by considering x-ray photoemission spectroscopy[1-5]. In this paper we show the proposed technique and how the technique gives us physical insight at nanoscale into the parameters contributing to e for polymorphous SiO2 with various e values. It is found that the e values are universally scaled in terms of r x dn, where r is the bond length and dn is valence charge difference of the initial and final state during photoemssion process.

[1] K. Hirose, et al, Appl. Phys. Lett. 93, 193503 (2008); [2] K. Hirose, et al, J. Phys. IV 132, 83 (2006); [3] K. Hirose, et al, Appl. Phys. Lett. 89, 154103 (2006); [4] K. Hirose, et al, Prog. Surf. Sci. 82, 3 (2007); [5] K. Hirose, et al, J. Phys. 100, 012011 (2008)

CM-4:IL10 Structure, Magnetic and Spintronic Characteristics of Sandwiched Metal-organic Clusters and Molecular Wires

Jinlan Wang*, Xiuyun Zhang, Liyan Zhu, Department of Physics, Southeast University, Nanjing, P.R. China

Organometallic sandwich clusters and wires TMn(FeCp2)n+1 and EunCOTn+1 are investigated using spin-polarized density functional theory. The total magnetic moments (MMs) of TMn(FeCp2)n+1 (TM=V,Ti,Mn) increases linearly with the size n. Tin(FeCp2)n+1 and Vn(FeCp2)n+1 exhibit giant MMs 4,8,12µB and 1,6,11µB, respectively for n=1-3. All the four molecular wires are ferromagnetic semiconductors with a relatively large band gap of 1.310eV for [Mn(FeCp2)]8 and a 5µB MM per unit cell for [V(FeCp2)]∝. The EunCOTn+1 are thermodynamically stable with freely rotatable COT rings. The total MMs can be generalized as 7n-2µB and the ferromagnetic state is energetically competitive with the anti-ferromagnetic state, meaning that the spin states are unstable. More importantly, we uncover an interesting bonding characteristic that the interior ionic structure is capped by two hybrid covalent-ionic terminals, which makes the EunCOTn+1 clusters extremely stable. We further reveal that for the positively charged clusters, the hybrid covalent-ionic terminals will tip further towards the interior part of the clusters to form deeper covalent-ionic caps. In contrast, the negatively charged clusters turn to pure ionic.

[1] X.Y. Zhang, et al, ACS Nano, 3, 537(2009); [2] X.Y. Zhang, et al, ACS Nano, 3, 2512 (2009)

CM-4:IL11 Models and Simulations of the Growth of Carbon Nanotubes

Shaun C. Hendy*, Dmitri Schebarchov, MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, Wellington, New Zealand; Aruna Awasthi, Industrial Research Ltd, New Zealand; Barry Cox, University of Wollongong, Wollongong NSW, Australia

Despite almost twenty years of endeavour, it is still not possible to grow single-walled carbon nanotubes with selected chirality. Unfortunately, there are few clues from theory to guide experiments in this area, which have largely relied on a trial and error approach. The growth process is difficult to simulate computationally, due to the complex chemistry and thermodynamics involved, and the long time scales associated with growth. Furthermore, there have been few attempts to develop quantitative models that provide insight into chiral selectivity. Here we report on the development of a model that focuses on the lift-off of the carbon nanotube cap after nucleation. We test the model using atomistic molecular dynamics simulations and discuss the implications of the model for understanding growth processes that may control chirality.

Session CM-5

R&D Advances in Devices and Applications

CM-5:IL01 Design of Biomolecule-nanoparticle Complexes for Highly Sensitive Biological Detection

Chunhai Fan, Shanghai Institute of Applied Physics, CAS, Shanghai, China

The use of gold nanoparticles (AuNPs) has a long history in biology, dating back to the application of “immunogold” in biological imaging in the 1970’s. Based one the unique optical and electronic properties of AuNPs, a series of methods for ultrasensitive detection of DNA and proteins by using AuNPs have been developed. This has motivated intense interest to develop AuNPs-based biodetection. Here I will present several examples from our group, demonstrating enhanced biodetection performance by exploiting nanoparticle-biomolecules interactions.

CM-5:IL02 Development of Carbon Nantube Alumina Composite and Their Application to Industrial Production

M. Omori*, G. Yamamoto, T. Hashida, Graduate School of Engineering, Tohoku University, Sendai, Japan; A. Okubo, H. Kimura, Institute for Materials Research, Tohoku University, Sendai, Japan

This presentation is related to the composite fabricated from multiwalled carbon nanotubes (MWNTs) and aluminum hydroxide. It is an idea to classify MWNTs into two kinds according to thickness of graphen sheets, namely, thick and thin MWNTs. There is great difference of stiffness between thin and thick MWNTs. Almost all composites have been prepared from thin MWNT, because suppliers of thick MWNT are limited. The composite prepared from two MWNTs was different associated with structure and mechanical properties. Thin MWNTs were agglomerated over 100 microns but not individualized in the composite matrix. Bulk density, Young’s modulus, bending strength and fracture toughness decreased steeply with increasing more than 1 mass% thin MWNT. Thick MWNTs were individualized in the composite and in addition, their agglomeration was observed. The size of the agglomeration depended on the added amount of thick MWNTs. The composite of 5 mass% thick MWNT consisted of the agglomerate near 10 microns in length. This dispersion meant to be more uniform than those of thin MWNTs. The steep drop of bulk density and Young’s modulus found in the composite of thin MWNT was eased by the uniform dispersion. The bending strength exceeded that of an alumina compact between 0.3 and 2 mass% thick MWNTs and decreased gradually over this range, being not less than 400 MPa. The toughness of the thick MWNT composite was beyond that of an alumina compact between 0.3 and 5 mass%.

CM-5:L03 The Ballistic Impact Characteristics of Woven Fabrics Impregnated with a Colloidal Suspension and Flattened Rolls

Chun-Gon Kim[1]*, Il-Jin Kim[1], Gun Lim[1], Byung-il Yoon[2], [1]Department of Aerospace Engineering, KAIST, Daejeon, Korea; [2]Agency for Defense Development, Daejeon, Korea

Nowadays, aramids and UHMWP(ultra high molecular weight polyethylene) have been used for personal body armor. These high performance fabrics have high strength, high energy absorption and low density. However, to protect projectiles from high velocity, ceramic or heavy mass of plate is inserted in the vest, which makes armor bulky and stiff. Therefore, lots of body armor researches have been focused on high strength fabric with nano materials that show the shear thickening behavior. It is a behavior with drastic increase in viscosity over a certain shear rate. For the study, the specimens of a neat Kevlar KM2 fabric and a KM2 fabric which was impregnated with SiO2 colloidal suspension were prepared. Ballistic impact tests were carried out for different shapes of projectiles and boundary conditions. Also suggested is the ballistic bumper design of flattened roll of unidirectional UHMWP, which can mitigate the impact energy to the rear fabric layers. The effect of flattened roll on impact energy absorption was investigated for various stitching conditions.

CM-5:IL04 Design of Nanostructured Sol-Gel Coatings for Targeted Applications

E. Scolan*, R. Pugin, S. Pasche, B. Wenger, G. Voirin, Centre Suisse d’Electronique et Microtechnique SA, Neuchatel, Switzerland

Sol-gel processes are very adapted and versatile to deposit layers with controlled homogeneity, thickness, porosity and associated surface structures. Moreover the room temperature wet conditions of the sol-gel processes are compatible with the loading and surface functionalisation of porous films with organic or biological entities. Based on sol-gel technology, morphological and chemical characteristics of the nanoporous layers have been adjusted according to the requirements for the final integration: from the choice of the metal oxide precursors (molecular to nanoparticulate), the formulation composition, to the fine adjustment of deposition process parameters, several nanoporous layers have been developed at CSEM to benefit from the paramount surface to volume ratio, the high pore volume, the designed pore sizes and the enhanced surface roughness. In this respect, sensitive layers have been developed for (bio)detection of soluble analytes, and for gas sensing. Moreover, enhanced printing properties, drug delivery, catalysis, optical effects (antireflective, luminescence), tuneable wetting properties (anti-fog, self-cleaning) have been achieved by the fine design of functionalised low cost sol-gel layers using industrially upscalable processes.

CM-5:IL06 Environmental Applications of Photocatalysis

Jimmy C. Yu, Department of Chemistry and Environmental Science Programme, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Materials at nanoscales possess interesting chemical and physical properties which can be exploited for environmental applications. When a photocatalyst is illuminated, it triggers an energetic response that can oxidize pollutants to environmentally acceptable products. For example, volatile organic compounds are degraded to carbon dioxide and water on illuminated titanium dioxide nanoparticles. TiO2 is an attractive photocatalyst because it is inexpensive and chemically stable. There is a serious limitation, however, that titanium dioxide requires excitation by UV and the process has a relatively poor quantum yield. Development of more effective photocatalysts is therefore crucial in the commercialization of this pollution treatment technology. A variety of approaches have been developed for improving the efficiency of titanium dioxide-based photocatalysts. These include metal and nonmetal doping, thermal and acid treatments, and sonochemical and microwave-assisted preparation. The enhanced photocatalysts show much improved activity but these powdered materials are still difficult to recycle in treatment facilities. To solve this problem, we have developed methods for coating photocatalytic thin films on inert substrates. These nanometer thin films have immense potential for water purification and air pollution cleanup. The strong oxidizing environment on the coatings also provides additional benefits such as anti-bacterial and superhydrophilic properties. To capitalize on these desirable properties, we work closely with industrial partners. Our NanoPCOT technology was commercialized and has been licensed for use in high-end water treatment and air purification systems. A number of non-TiO2-based semiconductors have also be fabricated and applied for photocatalysis by this research group.

CM-5:IL08 Preparing of Nano MLCC Powders for Ultrathin-layer BME-MLCC Application

X.H. Wang*, Y.C. Zhang, L.T. Li , State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing, China

Dielectric ceramics based on barium titanate BaTiO3 (in short BT) have been extensively studied since BT is a promising material especially for multilayer ceramic capacitors (MLCCs). As the thickness of the dielectric layer in the monolithic ceramic capacitor becomes as thin as 1 micrometer, in order to meet the reliability requirement, the grain size of ceramic grains in each layer should be reduced to around 100nm.The method of additive's doping has been found seriously influenced the microstructure and dielectric properties especially with decreasing particle size. The best doping method for nanograin BT powder is chemical coating technology, which results in well distribution of dopants around the BT particles and leads to more uniform microstructures and good dielectric properties of the ceramics. The objectives of this work are to research and prepare the ultrafine-grained X5R type BT based ceramic materials with high performance for next generation Ni-MLCCs application using chemical coating method, and to get better understanding of the issues involved in this project, such as chemical coating processing control, material formulation, microstructure, the size effect, sintering process and relative mechanism, respectively.

CM-5:IL09 A ZnO Nanorod Homojunction Light-Emitting Diode

X.W. Sun, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore

In this talk, we report our recent results on fabrication of reliable ZnO vertically aligned rod-based homojunction UV/visible light-emitting diodes. The nanorod were uniformly grown on both Si and sapphire substrates by metal catalyst-free vapor phase transport method, followed by As^+/ P^+ ion implantations and thermal activation to convert top layer of the intrinsic nanorod into *p*-type. Devices doped with either As or P ions give similar electrical and electroluminescence properties. Single homojunction nanorods have been probed by nanomanipulator and show typical rectifying behavior. The electroluminescence of as-prepared diodes shows a strong UV ZnO band-edge emission, which is still detectable five months after fabrication.

Poster Presentations

CM:P01 Room Temperature Fabrication of Highly Crystallized ZnO Thin Films on Polymer Substrates by using Nanosheet Seed Layer

T. Shibata*, T. Ohnishi, I. Sakaguchi, M. Osada, K. Takada, T. Sasaki, NIMS & JST-CREST, Tsukuba, Ibaraki, Japan; T. Kogure, The University of Tokyo, Tokyo, Japan

Thin film technology plays an important role in modern industries, and one of the most attractive issues in this field is design and control of crystalline film on inexpensive substrates such as glass and plastics. Recently, we proposed a novel method to control the film growth using unique two-dimensional (2D) crystals called "nanosheet" as a seed[1]. The nanosheets have been synthesized by exfoliating a layered compound and the obtained nanosheets can be tiled on substrates by simple solution-based processes. Thus, in this study, we applied this technique to attain well-controlled film deposition of functional crystal on polymer substrates. The nanosheet with 2D-hexagonal lattice was used as a seed. The nanosheet seed layer was fabricated using Langmuir-Blodgett deposition, and then, ZnO film was deposited at room temperature by pulsed laser deposition (PLD). XRD and TEM observations revealed that the obtained films were highly crystallized and oriented along the c-axis. Highly crystalline texture directly formed on top of the substrates, which has been realized for the first time. Drastic improvement of the film performance was successfully demonstrated by measuring the electrical conductivity of the films.

[1] *T. Shibata et al, Adv. Mater. 20, 231 (2008)*

CM:P03 Preparation of PVA/Sm2O3 Composites Nanofibers by Electrospinning Tecnique

P. Frontera*, C. Busacca, V. Modafferi, P.L. Antonucci, Dipartimento Meccanica e Materiali, Università Mediterranea di Reggio Calabria, Reggio Calabria, Italy; M. Lofaro, CNR-ITAE Institute, Messina, Italy

Nanostructured ceramic materials could replace all bulk ceramics in applications such as catalysis, fuel cells, solar cells, membranes, hydrogen storage batteries, in biology for tissue engineering, biomolecular machines, biosensors, etc. due to their high value addition. Besides, nanostructured ceramic oxides have potential applications in nanoelectronics, optical, sensor, resonator, and opto- and magnetoelectronic devices due to the physical properties coming from their electronic structure. The utilization potentiality of such ceramic nanostructures depends on the uniformity of their production. Besides, nanostructured ceramic oxides have potential applications in nanoelectronics. In this context the electrospinning technique appears a suitable method to produce nanofibers. In the electrospinning process, polymeric/ceramic solution is poured into a syringe equipped with a needle tip. When a high electric field is applied between the tip of the needle and the counter electrode (collector), a thin solution jet would be initiated from the tip of the needle and travels to the collector as the electrical force reaches a critical value to overcome the surface tension of the polymer solution. In this work PVA/Sm2O3 composite fibers were prepared by using electrospinning technique. The fibers obtained were characterized by scanning electron microscopy, X-ray diffraction, thermogravimetric analysis and Fourier transform infrared spectroscopy.

CM:P05 Growth Kinetics of Nanowires in Glass-ceramic with Rare Earths for Optical Data Storage

S. Jinga*, E. Andronescu, C. Jinga, Dept. of Science and Engineering of Oxide Materials, Politehnica University, Bucharest, Romania; E. Rotiu, L. Ionescu, C. Mazilu, National Glass Institute, Bucharest, Romania; E. Pavel, Storex Technologies, Bucharest, Romania

The paper presents the growth kinetics of nanowires having diameter smaller than 30nm in a fluorescent glass-ceramic and their application as optical data storage medium. The material was analyzed by HRTEM, SEM and photoluminescence spectroscopy. Nucleation rate and growth constant have been measured. The results were interpreted by a diffusion model.

CM:P06 Irradiation of a Nanocomposite of Pseudoboehmite-nylon 6,12

A.H. Munhoz Jr.[1], R. Meneghetti Peres[1], L.H. Silveira[1], L.G. Andrade e Silva[2], L.F. de Miranda[1], [1]Universidade Presbiteriana Mackenzie, Sao Paulo, SP, Brasil; [2]Instituto de Pesquisas Energeticas e Nucleares - IPEN

Nanocomposites are nanometrical material particles embedded in a specific matrix. The degree of organization of the nanostructures and their properties depend on the nature of the organic and inorganic components of the structure that can generate synergic interactions. Polymeric nanocomposites are related to a class of hybrid materials where inorganic substances of nanometric dimensions are dispersed in a polymeric matrix. In the present work nanocomposites of nylon 6,12 with different concentrations of pseudoboehmite obtained by sol-gel process were prepared with and without the presence octadecilamine. After preparation the samples were irradiated in irradiation doses of 100 kGy, 300 kGy, and 500 kGy in an electron accelerator. The pseudoboehmite nano particles were characterized by X-ray diffraction, scanning electron microscopy, differential thermal analysis and thermo gravimetric analysis. The nanocomposites were characterized by thermal and mechanical tests. The addition of pseudoboehmite promoted a reduction of the melting flow evidencing the interaction of pseudoboehmite with the polymeric matrix, modifying its crystalline structure.

CM:P07 **Synthesis of Photocatalytically Active Titania Nanoparticles**
Olga Mashtalir, Sergey Pogulay, Maksym Verovchuk, Alexey Gogotsi*, Materials Research Center, Kiev, Ukraine; Murat Kurtoglu, Isabel Knocke, Yury Gogotsi, Drexel University, Philadelphia, PA, USA

Titania nanoparticles are widely used in photocatalysis, solar cells, pseudocapacitors and other applications. This report is on a scalable method of synthesis of pure and nitrogen-doped anatase nanopowders with the particle size from several nanometers to more than 100 nm, which can be controlled by the process parameters. Preparation of nanosized titanium dioxide with the anatase structure was achieved by precipitation from solutions with subsequent calcinations. The reaction of the isopropanol solution of titanium tetrachloride with ammonia was used in the synthesis process. The effects of the process parameters (pH, temperature and time of calcinations) on the phase composition, particle size, color and morphology have been studied using XRD, Raman spectroscopy and TEM. Nitrogen doping leads to yellow powders. It is important to stress that titanium chloride produced as a chemical industry waste was used in this process. Nanosized TiO2 prepared by this method shows a strong photocatalytic activity. The prepared titania solutions were found to very active to degrade solutions of Methylene blue, Methyl Red and colored household chemicals under UVA light.

CM:P08 **Preparation of Perovskite-Type Niobate Nanosheets Having a Variable Thickness Composed of (NbO6)n Octahedron (n=4-6)**
Y. Ebina*, K. Akatsuka, T. Sasaki, National Institute for Materials Science, Tsukuba, Japan

Layered perovskite niobates of Dion-Jacobson series, KCa2Na(n-3)Nb(n)O(3n+1), have been chemically exfoliated to produce a unique class of niobate nanosheets with a thickness controllable at a step of NbO6 octahedron height. The starting layered materials of KCa2Na(n-3)Nb(n)O(3n+1) for n= 4-6 were prepared by repeated solid-state calcination of KCa2Nb3O10 (n=3 analog) and NaNbO3 at 1573 K. They were converted into protonic forms, which were reacted with a tetrabutylammonium hydroxide aqueous solution to produce turbid suspensions. Nearly perfect delamination was confirmed by XRD data on colloids centrifuged from them, which indicated the total loss of basal diffraction series and appearance of characteristic oscillating broad profiles. AFM observations detected unilamellar sheets with a thickness of 2.7 nm (n=4), 3.1 nm (n=5) and 3.6 nm (n=6), which are compatible with the number of corner-shared octahedra along the sheet normal. In-plane XRD data provided further evidence for the formation of the nanosheets as two-dimensional single crystals. In conclusion, we obtained the nanosheets, Ca2Na(n-3)Nb(n)O(3n+1) (n=4-6), having a variable thickness composed of (NbO6)n (n=4-6). These nanosheets are promising as a building block of high-performance photocatalysts and dielectrics.

CN - 6th International Conference

ADVANCED INORGANIC FIBRE COMPOSITES FOR STRUCTURAL AND THERMAL MANAGEMENT APPLICATIONS

Oral Presentations

Session CN-1

Production and Properties of Reinforcements, Preforms, and Matrix Materials

CN-1:IL01 **Advanced Ceramic Fibers**
D. Sporn, Fraunhofer-Institute für Silicatforschung, Wuerzburg, Germany

Due to the need to enhance the energy efficiency there is still a strong need to focus on the use of ceramic matrix composites within the hot parts of gas turbines. Such materials will offer important contributions to increase the energetic output that decreases at the same time the release of carbon dioxide. But, there is still a bottle-neck regarding the availability of ceramic fibers at reasonable prices. Therefore, the strengthening of the fiber development and the implementation of them within CMC is still an important issue. Several approaches have been proven in the past to implement ceramic fibers into the market. The state of the art is characterized by high quality SiC fibers derived from polycarbosilanes, these are available in small quantity at very high selling prices. The developmental targets focus on two important issues: first, the search of new compositions and/or microstructures that can survive at high temperatures, and, second, to develop alternative fiber fabrication routes starting from comparably low-cost precursors. The paper will cover the most important aspects starting from the precursor chemistry up the finally measurable fiber properties. On the hand of fiber compositions like SiBN3C and SiC it will be demonstrated, that alternative routes could be developed.

CN-1:IL02 **Composites with Ceramic Matrix Through Sol-gel Route**
S. Manocha*, Milan Vyas, L.M. Manocha, Department of Materials Science, Sardar Patel University, Vallabh Vidyanagar, India

The chemical synthesis of ceramics and glasses by sol-gel processes has become an area of significant importance in the field of materials science. The ability to infiltrate the sols into fibrous performs followed by insitu polymerization and subsequent heat treatment has given new dimensions to the ceramic matrix composites with tailored matrix chemical compositions. sols prepared using different composition of TEOS & CH3 functional group containing silane through hydrolysis-condensation process have been infiltrated into fibrous performs of carbon and silicon carbide. Specific attention is given on the fiber/matrix interactions since these matrices contain oxygen. The porous composites obtained through sintering are further infiltrated repeating the above process. However, the number of cycles could be reduced through addition of nanosize solids of the similar composition. The ultimate composites possess high fracture strength and desired fracture modes as compared to the composites prepared using conventional processing techniques.

CN-1:IL03 **Electrospinning of Ceramic Nanofibers**
Wolfgang Sigmund, University of Florida, Gainesville, FL, USA, and Hanyang University

Electrospinning and electrospraying are exciting novel approaches in the field of ceramics to synthesize a variety of nanostructures, be it nanoparticles, nanotubes, nanofibers, ribbons, or ceramic fiber mats. They appear to be amongst the most versatile processing strategies to achieve nanostructures under ambient conditions for many ceramics. This talk will be present a short overview of the history of electrospinning and recent advances in ceramic nanofiber synthesis. A novel method for testing the elastic modulus for nanofibers via atomic force microscopy will be discussed. Furthermore, these novel nanomaterials exhibit enhanced or novel properties that allow for applications in fiber composites.

CN-1:L04 **Si-C-O Fibers in Gas Reactive Atmospheres**
M. Brisebourg, G. Puyoo, H. Plaisantin, G. Chollon*, Laboratoire des Composites Thermostructuraux, University of Bordeaux, Pessac, France

The high temperature reactivity of Si-C-O fibres in various atmospheres is strongly related to their initial composition and structure. It apparently holds true for chlorine treatments, as the nanoporous carbon layer growth rate seems to depend on the relative proportions of free carbon, silicon oxycarbide and nanocrystalline SiC in the fibres. The aim of the present work was to correlate the carbon layer growth kinetics with the physico-chemical properties of a wide range of Si-C-O fibres. Large reaction rate disparities have been observed between the various materials. If a large amount of mixed silicon atom environments increases the reactivity of Si-O-C materials with Cl2, this sole feature does not explain all experimental results. The presence heteroelements (Ti, Zr, Al.) or large quantities of percolated free carbon both appear to bear on the reaction rate. For a better overall knowledge on the fibres reactivity, this study was extended to other model materials (oxycarbide glasses, SiC nanopowders) and gas reactive treatments (NH3.).

CN-1:IL06 Ceramic Fibers - Manufacturing, Properties and Applications

B. Clauß, ITCF Denkendorf, Denkendorf, Germany

Ceramic Fibers are one of the important components in ceramic matrix composites. Oxidic as well as non-oxidic fiber types are on the market and under development in research laboratories. Fibers can be produced via melt- or dry-spinning processes with subsequent pyrolysis and sintering/tempering steps. The structure formation and the final fiber performance strongly depends on the manufacturing conditions. The long time performance of oxide fibers at high temperature is limited by grain growth mechanisms, creep behaviour and corrosion effects. In the case of non-oxide fibers degradation via oxidation and undesirable crystallization effects are the limiting factors. Although the commercially available fibers have already good properties, further development is necessary to supply even more advanced fibers at reasonable prices. The different properties of oxide and non-oxide fiber types are complementary in many cases, so that each fiber class is suitable for interesting applications. Potential fields of application are aerospace, automotive and energy management.

CN-1:L07 Continuous Non-oxide Nanofibers Produced with a Polymer-derived Ceramic Approach

V. Salles*, S. Bernard, A. Brioude, D. Cornu, P. Miele, Laboratoire des Multimatériaux et Interfaces UMR UCBL/CNRS 5615, Université Lyon 1, Villeurbanne, France

A growing interest is given to electrospun nanofibers (NFs) for new potential applications as large as textile industry, nanomedicine, food industry, etc. New generation materials can be designed and then used in order to improve some specific properties according to the desired application. In the field of ceramics, many studies are dedicated to the elaboration of oxides, i.e. Al2O3, TiO2 and SnO2 for instance, but only a few articles deal with high-temperature non-oxide ceramics, like SiC and B4C. Moreover, in these latest studies, the authors pointed out the difficulty to keep the fiber shape after ceramization of the material. We propose to present boron-based ceramic NFs obtained from preceramic polymers, with a controlled shape and a high purity. The nature of the final ceramics is changed by varying the compositions of the starting boron-based polymers. The shape quality of the NFs is modified by adjusting the electrospinning parameters. Homogeneous cylindrical BN-NFs are finally obtained after a high-temperature treatment. Such electrospun NFs are potential candidates as reinforcing agents in ceramic matrix not only to increase the thermomechanical properties of a ceramic material, but also to create “multi-functional” materials.

Session CN-2
Processing and Fabrication

CN-2:IL01 Fabrication, Microstructures, Mechanical Properties and High Temperature Performance of Tungsten Matrix Composites Reinforced by TiC and ZrC Particles

Yu Zhou*, Yujin Wang, Guiming Song, Taiquan Zhang, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, China

This paper summarized the research results of refractory metal carbides reinforced tungsten matrix composites investigated by our group in Institute for Advanced Ceramics, Harbin Institute of Technology in the last decade. The two kind of TiCP/W and ZrCp/W composites were prepared by vacuum hot-pressing. The microstructure, and properties, such as room and elevated temperature mechanical properties, thermo-physical properties, thermal shock and ablation resistance of the composites were studied in details. The thermodynamic and chemical consistency between different phases is excellent in the composites. In TiCp/W and ZrCP/W composites, W atoms diffused into the lattice of TiC or ZrC during the sintering process, forming (Ti,W)C and (Zr,W)C solid solution, respectively, which increases the bonding strength of interface and promotes the densification of composites. The incorporation of carbide particles inhibited the grains growth of W matrix and obviously improved the mechanical properties, thermo physical properties and ablation resistance of the composites. The ZrC particles can strongly inhibite the plastic deformation of tungsten matrix at high temperatures. The coordinated deformation of ZrC particles over 1200 °C was found in the ZrCp/W composites. The deformation mechanism of ZrCp/W composite is dynamic recovery in tungsten-matrix at temperatures below 1500 °C, as well as dynamic recrystallization at 1600 °C. High temperature strengthening mechanisms in ZrCp/W composites mainly consist of fine grain strengthening, interface strengthening, geometrically necessary dislocations strengthening, and loading transition strengthening. The tungsten matrix composites have been used extensively as holding devices and anvils of high temperature equipment, even showing great potential applications in the airspace area.

CN-2:L03 Hierarchical SiC-based Ceramic Matrix Composites Reinforced with SiC Nanowires Grafted Carbon Fibers

B. Lu[1, 3]*, S.M. Dong[1, 2], Z. Wang[1, 2], X.Y. Zhang[1, 2], Y.S Ding[1, 2], [1]Structural Ceramics and Composites Engineering Research Center, Shanghai Institute of Ceramics, CAS, Shanghai, P.R. China; [2]State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, CAS, Shanghai, P.R. China; [3]Graduate University of Chinese Academy of Sciences, Beijing, P.R. China

Hierarchical SiC-based ceramic matrix composites with highly sophisticated structures were synthesized by a combination of Chemical Vapor Infiltration (CVI) and Polymer Infiltration and Pyrolysis (PIP) methods. Large amount of SiC nanowires were in-situ grown on the surface of carbon fibers by CVI process, and then embodied in SiC matrix by PIP densification. The incorporation of SiC nanowires in the composites introduces both nanometer-scale reinforcements and interphase with expectations to decrease the flaw sizes as well as provide more crack deflection networks, which makes the composites less flaw-sensitive and less crack-sensitive, result in extra reinforcements on the strength and fracture toughness of composites. The mechanical properties of hierarchical composites were characterized and compared with conventional carbon fiber reinforced SiC matrix composites. The nanometer-scale strengthening and toughening mechanisms were preliminarily studied.

CN-2:IL04 Effect of Nanoreinforcements on Structure and Properties of Carbon/Carbon Composites

L.M. Manocha*, R.B. Pande, Vishal Mankadia, S. Manocha, Department of Materials Science, Sardar Patel University, Vallabh Vidyanagar, India

The gap between the desired and achievable properties and those of the achieved ones resulted in continuous R&D in the field of reinforcing materials. The recent development of nanomaterials, the so-called carbon nanostructures like fullerenes, carbon nanotubes and carbon nanofibers as well as carbon nanoparticles, nanocapsules and the recent much talked grapheme have renewed interest in composites. Amongst these, study of carbon nanotubes as reinforcing material is one of the main areas of focus due to their combine mechanical and thermal characteristics. The present work described the synthesis of multiwall carbon nanotubes (MWCNTs) alone as well as on the surface of fiberous substrate by chemical vapour deposition method using Fe (NO3)2 and Iron (III) as catalyst precursors and xylene as carbon source. High purity multiwall carbon nanotubes were also grown on carbon fibers, silicon carbide cloth by decomposition of ferrocene -xylene solution into a reaction furnace by chemical vapour deposition (CVD) method. The grown carbon nanotubes were randomly as well as vertically aligned in high density on a large area of the substrate. These have been further used as reinforcements with carbon as matrix using CVI technique as well as solution technique. The addition of graphene into the carbonaceous precursors gives additional dimension to the reinforcement which is found to affect the microstructure as well as properties of the ultimate carbon/carbon composites.

CN-2:IL05 Microstructures and Properties of Ultra-high-temperature Ceramics (UHTCs) based Composites with Carbon Fibers as Reinforcements

Shaoming Dong, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China

In order to fabricate carbon fiber reinforced UHTC matrix composites with a homogeneous distributon of UHTC phases, UHTCs-containing slurry infiltration and in-situ synthesized ZrC through carbothermal reduction were employed to introduce UHTC phases into the matrix of composites. The preparation conditions were optimized in order to obtain UHTC-based composite with excellent properties. High-temperature performances of UHTC based carbon fibers were examined by iso-thermal oxidation in muffle furnace at high temperatures and by oxyacetylenic flame ablation. Microstructures and mechanical properties of composites both before and after high temperature examination were analyzed for comparison.

Session CN-3
Laminated Composite Structures

CN-3:IL01 **Design and Preparation of Laminated Composites**
Dongliang Jiang, The State Key Lab of High Performance Ceramics and Superfine Microstructure Shanghai Institute of Ceramics, CAS, Shanghai, China

Active researches have been conducted to seek the application of ceramics as structural components; however, the lack of damage tolerance ability has been a critical problem. Laminated composites as one of the main way for improving the brittleness of ceramics are getting more and more attention from the biomimetic point. Clegg and co-workers have produced laminated SiC with graphite interface layers. These multilayer SiC composites showed stepped stress-strain behavior with well improved mechanical properties. Recently, it was shown that laminated composites without weak interfaces also exhibited damage-tolerant behavior. In the present paper, SiC/TiC and ZrB2-SiC/ZrB2 laminated composites were prepared through aqueous tape casting, laminating and hot pressing. The rheological properties of tape casting slurries were characterized and the tape casting process was optimized. The finite element method (FEM) was used to design a symmetrical layered structure with gradual thermal residual stress distribution. The surface stress conditions of the sintered ceramic were tested by X-ray stress analysis. The dependence of mechanical properties (fracture strength and toughness) on the structural parameter (the composition of layers, the thickness ratio between layers, number of layers) was investigated. The strengthening and toughening mechanisms of the ceramics were also studied.

CN-3:IL02 **Joining and Integration of Ultra High Temperature Ceramic Composites**
R. Asthana*, Department of Engineering and Technology, University of Wisconsin-Stout, Menomonie, WI, USA; M. Singh, Ohio Aerospace Institute, NASA Glenn Research Center, Cleveland, OH, USA

There is growing interest in the development of transition metal diboride-based ultra high temperature ceramic composites (UHTCCs) for use as TPS components of space vehicles. Robust joining and integration technologies shall play a key role in hierarchical manufacturing of complex parts based on these difficult-to-machine composites. We developed and demonstrated advanced joining concepts and brazing technology for integrating ZrB2-based composites to themselves and to Ti, Inconel, and Cu-clad-Mo using a variety of Ni, Cu, Ti, and Pd-base amorphous and crystalline braze alloys with melting temperatures as high as 1510 K. We focused on brazing response of three hot-pressed ZrB2-based ultra-high-temperature composites, ZSS, ZSC and ZS (Z: ZrB2, S: SCS9a SiC fiber or SiCp, C: carbon) containing SiC particulates and either carbon powder or SCS9a silicon carbide fibers. Microstructural characterization of as-fabricated joints was performed using optical microscopy, SEM, and EDS. The joints were characterized using Knoop micro-indentation testing to develop hardness distribution and assess the residual stress state and joint integrity following brazing. In this presentation, the role of braze composition, composite constituents, and joining conditions on joint microstructure, chemistry, microhardness, residual stress and thermal resistance of ZrB2-based composites joined to themselves and to Ti, Inconel, and Cu-clad-Mo will be presented.

CN-3:IL03 **Damage-tolerant Laminate-type Hybrid Ceramics**
Yutaka Kagawa, Research Center for Advanced Science and Technology (RCAST), The University of Tokyo and National Institute for Materials Science (NIMS), Tokyo, Japan

Laminate type hybrid type ceramics, composed of CFCCs and monolithic ceramics, have been designed and potential of the hybrid ceramics have been examined. All oxide Al_2O_3 fiber/Al_2O_3 matrix CFCC- Al_2O_3 monolithic hybrids and SiC fiber/ZrB_2-CFCC-ZrB_2 monolithic hybrids are fabricated and these hybrids are subjected to mechanical tests. Fracture behaviors of the hybrid ceramics under various mechanical loading conditions are observed both micro- and macro-levels. The hybrid ceramic materials show damage tolerant behavior with a small expense of toughness and strength. Merits of hybrid ceramics are discussed through comparison of fracture behaviors between monolithic and hybrid ceramics. Future trend of hybrid ceramics is also discussed.

CN-3:L04 **Optomechanical Borosilicate Glass Matrix Composites**
Bo Pang*, David McPhail, Aldo R. Boccaccini, Department of Materials, Imperial College London, London, UK

The reinforcement of glass with ceramic fibres or particles is a common approach to improve the thermo-mechanical and functional properties of this material.In this investigation, alumina fibre reinforced borosilicate glass matrix composites were developed by hot-pressing. The transparency of the composites was achieved by introducing optical windows. The composites light transmittance was calculated in dependence of fibre spacing using a new equation derived from previous models available in the literature. In addition, in separate experiments, ZrO2 coated fibres were introduced as reinforcement with the aim to improve the mechanical properties of the composites. It was anticipated that the zirconia coating would introduce optimal fibre/matrix interfaces leading to improved fracture behaviour. The zirconia coating was obtained by a newly developed sol-gel process. The microstructure and chemistry of the interfaces between the matrix and fibres were investigated using a range of techniques, including SEM and SIMS. Overall, the new composites represent attractive transparent materials for possible applications in impact resistant windows for blast and ballistic protection. Further mechanical properties are required in future experiments.

Session CN-4
Property, Modeling and Characterisation

CN-4:IL01 **Interfaces and Interphases in Ceramic Matrix Composites: Influence on Mechanical Properties and Lifetime at High Temperature**
Jacques Lamon, CNRS/Université de Bordeaux, Laboratoire des Composites Thermostructuraux, Pessac, France

The fiber/matrix interfacial domain is a decisive constituent of fiber reinforced ceramic matrix composites (CMCs). It consists of the fiber/matrix interface or the fiber coating. Depending on characteristics of this domain, the composite will be either a brittle ceramic or a damage tolerant composite with tailored properties. Thus, several requirements, that may appear to be opposite, have to be met to obtain high performance composites. This paper discusses the concept of tailored interfacial domain in SiC/SiC composites, i.e. the main features of the interfacial domain with respect to composite mechanical properties, not only from a qualitative but also a quantitative point of view. The mechanics of matrix crack deviation are discussed. Criteria for cracking in the interface or within the interphase are proposed. Then, the influence of the interface or interphase crack on the stress-strain relation, fracture toughness, creep, static fatigue, etc., is addressed. Experimental data as well as predictions are shown. The techniques of measurement of interfacial characteristics are outlined. Data on these characteristics are provided. Finally guidelines for tailoring the interfacial domain and selecting the appropriate characteristics of fiber, interphase and matrix are discussed.

CN-4:IL02 **Modeling Tools for CMC Materials**
Dietmar Koch, Advanced Ceramics Group, University of Bremen, Bremen, Germany

Ceramic Matrix Composites (CMC) with fiber reinforcement provide an exemplary way to reduce the negative effects of brittleness of engineering ceramics, while the further advantageous properties of ceramic structures are retained. Additionally, they benefit from their low density and their excellent specific properties. Fundamentally, all CMC materials, both oxide and nonoxide composites, achieve enhanced fracture toughness and failure tolerance by incorporation of a sufficiently weak phase. This may be either a reduced fiber matrix interphase which allows fiber bridging of matrix cracks, or alternatively a weak matrix which enables crack branching and therefore prevents premature fiber failure. These diverse microstructures induce different mechanical properties and demand adopted modeling tools for accurate prediction of mechanical behavior of CMC components. The model approaches may be subdivided in micro-, meso-, and macromechanical modeling. For comprehensive calculation properties of fiber, matrix, and interface as well as - in case of delocalized failure - an integral evaluation of the composite properties have to be identified. The resulting finite element analysis is used for transfer of modeling results to design of complex components under real application conditions.

CN-4:L04 **Investigation of Thermal Properties of 3D- C/SiC Composites**

Ping He*, Shaoming Dong, Le Gao, Yusheng Ding, Xiangyu Zhang, Shanghai Institute of Ceramics, CAS, Shanghai, China

Carbon fiber reinforced silicon carbide (C/SiC) composites are promising materials for a severe thermal-erosive environment. 3D-C/SiC composites were fabricated by Chemical Vapour Infiltration and Polymer Infiltration and Pyrolysis (CVI+PIP) combined process. Coefficient of thermal expansion (CTE) and thermal conductivity of the composites were determined in in-plane and through-thickness direction, the CTE in the temperature range from room temperature to 1200 °C varies in the range (0.12~1.79) ×10-6/K in the through-thickness direction and (0.12~3.36) ×10-6/K in in-plane direction respectively, the thermal conductivity is 4.0W/m.k in the through-thickness direction and 9.26W/m.k in in-plane direction at room temperature. An extensive microstructure study was also carried out to understand the thermal properties of the composites. It was found that the thermal properties are closely related to the SiC fraction of the composites.

CN-4:IL06 **High Temperature Creep of Metal- and Ceramic-matrix Composites**

S.T. Mileiko, Inst. of Solid State Physics of RAS, Chernogolovka, Russia

Metal- and ceramic-matrix composites can be effective heat resistant materials provided their creep properties at temperatures 1100-1600°C are well controlled. To avoid too bulky physical experiment, micromechanical modelling should complement the experiment. The paper presents a system of the micromechanical models of the composites covering a number of creep mechanisms. Results of creep experiments performed on oxide-fibre/nickel-based-matrix composites at temperatures up to 1200 °C are also presented. Taking this type of composites as an example, an effectiveness of an approach to the development of creep resistant high temperature composites combined experimental and theoretical methods is shown. In particular, it has yielded a development of composites with a density of ~6.7 g/cm3 and creep resistance of 150 MPa at 1150 °C.

CN-4:IL07 **Modeling Infiltration of Fiber Preforms From X-ray Tomography Data**

G.L. Vignoles*, W. Ros, I. Szelengowicz, University Bordeaux 1, LCTS, Pessac, France; C. Mulat, C. Germain, M. Donias, University Bordeaux, IMS, Talence Cedex, France

The production of high-quality Ceramic-Matrix Composites often involves matrix deposition by Chemical Vapor Infiltration (CVI), a process which involves many phenomena such as gas transport, chemical reactions, and structural evolution of the preform. Control and optimization of this high-tech process are demanding for modeling tools. In this context, a numerical simulation of CVI in complex 3D images, acquired e.g. by X-ray Computerized Microtomography, has been developed. The approach addresses the two length scales which are inherent to a composite with woven textile reinforcement (i.e. inter- and intra-bundle), with two numerical tools based on random walks. The small-scale program allows direct simulation of CVI in small intra-bundle pores. Effective laws for porosity, surface and transport properties as infiltration proceeds are produced by averaging. They are an input for the next modeling step. The second code is a large-scale solver which accounts for the locally heterogeneous and anisotropic character of the pore space. Simulation of the infiltration of a whole composite material part is possible with this program. Validation of these tools on test cases, as well as some examples on actual materials, are shown and discussed.

Session CN-5
Composites for Thermal Management

CN-5:IL01 **Integration of High Conductivity Carbon Based Materials for Thermal Management Applications: Technical Issues and Challenges**

Mrityunjay Singh*, Andrew L. Gyekenyesi, Ohio Aerospace Institute, NASA Glenn Research Center, Cleveland, OH, USA; Rajiv Asthana, Department of Engineering & Technology, University of Wisconsin-Stout, Menomonie, WI, USA

Light-weight and high-conductivity carbon-carbon composites and graphitic foams are attractive materials for thermal management applications in a wide variety of heat sinks and heat exchangers. The increased fluid/surface contact area together with low weight-volume ratio and high ligament and bulk conductivities of graphitic foams offer increased thermal efficiency in such devices. Integrating high conductivity C-C composites and graphite foams in airborne thermal systems requires robust and thermally conductive joints between composite, foam, and metals. In this study, high conductivity carbon-carbon composites as well as graphitic foams with different densities were vacuum brazed to titanium, Cu-clad-Mo, and Inconel-625 using AgCuTi braze, Cusil-ABA. The joint microstructure and composition were examined to evaluate the joint integrity and stability, chemical interaction and diffusion, and the extent of braze penetration all of which influence the thermal response of the assembly. The effective thermal resistance of graphitic foam/Ti, graphitic foam/Cu-clad-Mo, and graphitic foam/Inconel-625 joint interface was estimated using 1-D, steady-state heat conduction analyses for planar and cylindrical geometries. The effects of foam and metal substrate conductivities, penetration by molten braze into pores, and the metal-to-foam thickness ratio on the overall thermal resistance of joined assemblies was evaluated.

CN-5:IL02 **Processing and Thermomechanical Properties of Copper-Carbon Nanofibres Composites for Thermal Management Applications**

Jon M. Molina-Aldareguia*, Fundación IMDEA-Materiales, Madrid, Spain; José M. Córdoba, Magnus Odén, IFM, Linköping University, Linköping, Sweden; Javier Tamayo-Ariztondo, María R. Elizalde, CEIT and Tecnun, San Sebastián, Spain; E. Neubauer, AIT - Austrian Institute of Technology GmbH, Seibersdorf, Austria

From a theoretical point of view and due to the properties of the constituents, carbon nanofibre (CNF) reinforced Cu composites offer a large potential as heat sink materials with a controlled coefficient of thermal expansion. However, to achieve their theoretical potential, several difficulties must be overcome to process this new class of composite material, such as the anisotropic properties of the CNFs, the dispersion of the CNFs into the Cu matrix, the fabrication of fully dense composites without degradation of the CNFs, as well as the optimization of the Cu-CNF interface. To study this, several types of carbon nanofibres (CNF) were coated with a uniform and dense copper layer by electroless copper deposition, with and without the addition of Cr interlayers in order to modify the interfacial properties. The coated fibers were then sintered by different solid-state sintering methods. Overall, strong variations of the thermal conductivity of the composites were observed (20-200 W/mK) as a function of CNF type, CNF volume fraction and Cr content, while the coefficient of thermal expansion (CTE) was found to be considerably lower than Cu (9-11 ppm/K). This paper gives an overview of these results, underlying the main challenges and potential of these new materials.

CN-5:L04 **Low Cost Carbon Fiber Based Composites**

K. Kowbel, FMC, Tucson, AZ, USA

FMC has a patented method to produce low cost Carbon-carbon and carbon-SiC composites. These composites are produced via a polymer method with an active filler. As a result the number of densification cycles required to achieve acceptable mechanical and thermal properties is greatly reduced. Mechanical and thermal properties of these low cost composites will be presented. In addition a plethora of commercial applications will be discussed which result from low cost, high quality composite processing. Specific applications include industries ranging from aerospace to solar energy.

CN-5:IL05 **Atomistic Scale Thermal Transport in Composites and Their Interfaces**
Ajit K. Roy, Air Force Research Lab., Materials and Manufacturing Directorate Thermal Sciences and Materials Branch (AFRL/RXBT), Wright-Patterson AFB, OH, USA

Aircrafts use its fuel as its primary heat sink in managing thermal load. The thermal loads have steadily increased to the upper temperature limit of the electronics in numerous operations scenarios; thus limiting the system performance. The thermal load is anticipated to increase even more in future systems that need to be addressed. The above system requirements demand significant improvement in the thermal efficiency of heat exchanger or any active cooling systems. It is known that materials interface and its configuration is extremely important in transporting thermal energy as the phonon transport through the materials interface dictates the transport efficiency. Similarly, the thermal transport in heterogeneous materials systems, such as composites, is essentially controlled by the phonon scattering phenomena at the materials interfaces due to materials property mismatch. Such phenomena are also prevalent in joints or component interfaces. In this work, the mechanism of thermal transport in aerospace composite, particularly at the atomistic scale will be discussed. The rational for the atomistic scale thermal interface tailoring will be illustrated with an example of a durable thermal interface concept applicable to adhesive joints.

CN-5:IL06 **Design Aspects and Requirements of Ceramic Matric Composites (CMC´s) for Space Engines**
S. Beyer[1]*, S. Schmidt[1], C. Wilhelmi[2], M. Bouchez[3], [1]Astrium Space Transportation, Munich, Germany; [2]EADS Innovation Works, Munich, Germany; [3]MBDA, Bourges, France

Various technology programmes in Europe are concerned with preparing for future propulsion technologies to reduce the costs and increase the life time of components for liquid rocket engine components. One of the key roles to fulfil the future requirements and for realizing reusable and robust engine components is the use of modern and innovative materials. One of the key technologies which concern various engine manufacturers worldwide is the development of fibre-reinforced ceramics, CMC's (Ceramic Matrix Composites). The advantages for the developers are obvious, the low specific weight, the high specific strength over a large temperature range, and their good damage tolerance compared to monolithic ceramics make this material class extremely interesting as a construction material. To use the CMC´s for space engines, a number of design aspects and requirements have to be taken into account. Besides the knowledge about the reproducible production of CMC´s, the understanding and justification of the material in relevant environment like gas compositions (species), temperatures, gas velocities and pressure conditions are indispensable for the design of a CMC product. To fulfil the technical requirements the engineers have to be justifying the life-time limits of the ceramic material in the appropriate environment. A new kind of test rig is developed and evaluated to test different materials and coating systems in harsh environment. This paper gives an overview of the evaluation and justification of C/SiC, C/C and C/C-SiC materials and different Environmental Barrier Coatings (EBC´s) for ultra high temperatures like CVD SiC, and ZrB_2, and HfC.

This work is a cooperative effort between MBDA France, EADS Astrium Germany and France and EADS Innovation Works Germany.

CN-5:L07 **Mechanical Properties of High Thermal Conductivity Silicon Nitride *In-Situ* Composite**
You Zhou, Kiyoshi Hirao, Tatsuki Ohji*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Dielectric ceramics are now widely used as substrates for a variety of electronic devices such as integrated circuits (IC). Considerable heat is generated in these devices, particularly recently developed high-frequency transistors and high-power ICs. In addition a thick copper wiring board is directly bonded to the substrates for conveying high electric current, which in turn causes large residual stresses. Therefore, the ceramic substrates are required to have good mechanical properties as well as high thermal conductivities. Silicon nitride is considered as one of the most potential candidates for such ceramic substrates, due to its excellent mechanical property and potential thermal conductivity. This paper deals with mechanical properties of high thermal conductivity silicon nitride ceramics where large fibrous grains are entangled and embedded in fine grain matrix (*in-situ* composite). The samples are prepared via reaction-bonding and post-sintering using a high-purity Si powder doped with Y_2O_3 and MgO as sintering additives. Nitridation was carried out at 1400 °C for 8 h, subsequently followed by post-sintering at 1900 °C for various times ranging from 3 to 24 h. Mechanical properties are evaluated by four point bending strength and fracture toughness measurements. When the sintering time increases, the grains become coarser with higher aspect ratio. With this microstuctural change, the thermal conductivity and the fracture toughness also increase while the bending strength decreases. The samples sintered for 12-24 h showed high fracture toughness (>10 $MPam^{1/2}$) and relatively good strength (500-600 MPa), in addition to high thermal conductivity (120-130 W/m/K). It is indicated that the reaction-bonding and post-sintering technique is a promising approach for fabricating silicon nitride ceramics with both high thermal conductivity and good mechanical properties at low cost.

CN-5:L08 **The Development of Alumina-based Ceramic Matrix Composites for the SHEFEX II Thermal Protection System (TPS)**
Peter Mechnich*, Bernhard Kanka, Martin Schmücker, DLR Institute of Materials Research, Cologne, Germany; Burkard Esser, DLR Institute for Aerodynamics and Flow Technology, Cologne, Germany

Various TPS panels were developed and manufactured from WHIPOX-type alumina/alumina ceramic matrix composites for DLR's SHEFEX II mission (Sharp Edge Flight Experiment). These CMCs have favorable properties such as high-temperature oxidation resistance and damage tolerance. A special feature of these CMCs is their inherent transparency for electromagnetic waves, making them attractive as thermal protection for antenna. Scheduled for autumn 2010 the SHEFEX II payload will perform an actively controlled atmosphere re-entry at a maximum velocity of Mach 11 where a high thermal load on the TPS is anticipated. Since emittance of alumina is low radiation cooling capability of alumina-based TPS panels is limited. In order to prevent thermal overload, emittance of CMCs was improved by coating and superficial impregnation with an oxidation-resistant CoFe-spinel. Thermal performance and material stability was evaluated in an arc-heated wind-tunnel at DLR. It turns out that the CoFe-spinel surface modification can reduce overall CMC temperatures by more than 200 K in a Mach 6 hypersonic flow field. The modified CMC exhibits microstructural stability up to an estimated TPS peak temperature of 1300 °C. Design and set-up of the SHEFEX II WHIPOX-type TPS panels will be presented.

Session CN-6
Applications

CN-6:IL01 **Carbon/Carbons and Their Industrial Applications**
Roland Weiss, Schunk Kohlenstofftechnik GmbH, Heuchelheim, Germany

The industrial application of carbon/carbon-composites is mainly dominated by two different application fields. The highest market volume is required for break lining systems for aircraft as well as for luxury passenger cars. Whereas carbon/carbons for aircraft break disks are commercially successfull, C/C-SiC disks for automotive industry are still a non-profit business. Market requirements and potentials of cost reduction will be discussed. In the field of composites, especially photovoltaic and semiconductor industries have to be considered the most growing market within the last years as well as in the near future. A broad variety of composites as to materials and costs is required. Carbon/carbons can fulfill all these different requirements due to the broad variation of carbon/carbon materials, due to the manyfold manufacturing techniques, the variety of reinforcement patterns as well as various post treatments. The influence of fibres, reinforcement patterns, matrix systems and manufacturing paramteters will be dicussed in detail.

CN-6:IL02 **CMCs for Friction Applications**
Walter Krenkel*, Herbert Mucha, Nico Langhof, Ceramic Materials Engineering, University of Bayreuth, Bayreuth, Germany

Ceramic Matrix Composites (CMCs) have already demonstrated their superior thermomechanical and frictional properties in high performance and lightweight brake systems. As the frictional requirements on the brake systems (automotive, conveying systems, lifts, etc.) differ widely, the material's properties have to be tailored for the diverse applications. Prior demands are high and stable coefficients of friction, low wear rates, high thermal conductivities and at least moderate strength levels. In principle, carbon-fibre reinforced SiC-composites (C/SiC), manufactured by the melt-infiltration of liquid silicon into carbon performs (LSI-process), can be modified in a wide range. Friction linings as well as brake disks have been developed and were investigated by tribological tests. Modifications of the constituents physical properties attempt to reveal performance relevant parameters. This covers e.g. variations of the pads' surface temperatures via different thermal conductivities, i.e. by usage of C-fibre types with differing thermal properties (heat capacity, thermal conductivity). Variations of fibre orientation ranging from short fibre to 0/90° oriented carbon fiber weave affect the pad's delamination sensitivity and heat transfer into the lining's bulk. The relationship between process parameters, microstructures and properties of C/SiC composites are discussed.

CN-6:IL03 **SA-Tyannohex-based Composites for High Temperature Applications**

Toshihiro Ishikawa, Ube Industries, Ltd., Ube, Japan

To modify the relatively low fracture toughness of monolithic ceramics, the incorporation of long ceramic fibre within a matrix material has been extensively performed. In this case, as cracks form in the matrix material and approach the fibres, they will be deflected at the interface between the fibre and the matrix. We developed another approach toward improving the toughness of ceramics involving the creation of a textured internal structure within the ceramic itself. Actually, we developed a tough ceramic, which consists of a highly ordered, close-packed structure of very fine hexagonal columnar fibres with a thin interfacial carbon layer between fibres. The interior of the fibre element was composed of sintered beta-silicon carbide crystal. This concept is fundamentally different from that described previously, in that it is extremely difficult to distinguish separate "fibre" and "matrix" phases in the traditional composite sense. The toughness of the material in this case derives from the tremendous amount of interface area created within the internal structure through the close packing of the hexagonal columnar fibres. Furthermore, this ceramic also achieved excellent high temperature properties, high thermal conductivity and low density.

CN-6:IL04 **Modeling and Characterization of SiC/SiC Composites for Aerospace Applications**

J.A. DiCarlo, NASA Glenn Research Center, Cleveland, OH, USA

In comparison to the best metallic materials, SiC/SiC ceramic composites offer the opportunity of aerospace engine components with reduced weight and higher temperature operation, with corresponding improvements in engine cooling requirements, emissions, thrust, and specific fuel consumption. Although much progress has been made in the development of advanced SiC/SiC constituent materials and processes, major challenges still remain for their implementation into these components. The objectives of this presentation are to briefly review (1) potential SiC/SiC aerospace components and their generic material performance requirements, (2) recent progress at NASA and elsewhere concerning advanced constituents and processes for meeting these requirements, (3) key SiC/SiC component implementation challenges that are currently being encountered, and (4) on-going modeling and characterization activities within NASA that are addressing these challenges.

CN-6:IL05 **Carbon/Carbon Brake Materials**

Peter Filip, Center for Advanced Friction Studies, Southern Illinois University, Carbondale, IL, USA

Brakes are designed to slow down or stop a vehicle by converting major part of its kinetic energy into heat by mechanism of friction. Carbon/Carbon (C/C) brake materials are composites consisting of carbon fibers embedded in a carbon matrix. Their light weight, excellent physical (mechanical and thermal) properties, and very reasonable friction and wear characteristics make C/Cs an excellent candidate for brake materials used for high energy braking applications such as in aircraft and Formula 1 racing cars. This review will address processing parameters of C/C brake materials, the resulting microstructure of carbon composites, and the related most important properties determining performance of C/C brakes used for aircraft and Formula 1. Factors influencing the coefficient of friction and its variability, brake wear, moisture challenges, and oxidation protection strategies will be reviewed and discussed. Fundamentals of testing and design of C/C brakes will also be addressed.

Poster Presentations

CN:P01 **Application of Fibre Produced by Plasma Spray Method in Cementitious Composition**

R. Dickuviene*, K. Brinkiene, J. Cesniene, R. Kezelis, Lithuanian Energy Institute, Kaunas, Lithuania

Strong interest is demontrated in utilization of waste catalyst produced by petrochemical industry. It might be reused as a fine additive in grouts for various purposes as castables, concrete mixing, bricks and other composition. Also it can be recycled into the fibres using thermal plasmas. Microstructure of fibrous material produced by employing non-equilibrium plasma spaying technology at atmospheric pressure was annalysed as well as possibility of application of produced fiber in cementitious composition. The influence of plasma spray regimes as well as annealing temperature on microstructure of the formed fibre was analysed. Also fiber interaction with cementitious complex binder and with each component of binder separately was investigated. SEM-EDS, DTA and XRD technique were applied to study morphology and composition of the fibres as well as reinforced complex binder.

CN:P02 **Irradiation of a Polypropylene-glass Fiber Composite**

L.H. Silveira[1], L.G. Andrade e Silva[2], L.F. Miranda[1]*, [1]Universidade Presbiteriana Mackenzie, São Paulo, SP, Brazil; [2]Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP), Brazil

Reinforced thermoplastics materials are widely used in the polymer industry, and one important example in these composites are the polypropylene and the glass fibers composite. The irradiation can promote alterations in the polymeric chains by scission and reticulation reactions. The purpose of this work is to study the effect of ionizing radiation in the properties of a polypropylene glass fiber composite. The pellets of 1,3cm length, containing 15% weight of oriented long glass fibers were obtained by extrusion, after that the corps for the mechanical and thermal tests were molded by injection, and finally irradiated. The mechanical properties (tensile strength, Izod impact) and thermal properties (HDT and Vicat) of the irradiated and not irradiated samples were obtained. The Irradiation doses of the samples were 30, 50 and 100kGy. The results show a decrease in the thermal and mechanical properties indicating a degradation of the polymeric matrix.

CN:P03 **Numerical Modelling of SiC-Matrix Composite Production by Liquid Silicon Infiltration Process**

A.V. Kulik*, V.I. Kulik, Yu.V. Zagashvili, Baltic State Technical University, St.Petersburg, Russia; M.S. Ramm, S.E. Demin, Reseach-and-production company "Ceracom" Ltd, St. Petersburg, Russia

Reaction sintering is a cost-effective method for making SiC ceramics such as Cf/C-SiC ceramic-matrix composites (CMC). Traditionally, the fabrication of SiC ceramics by reaction sintering involves Liquid Silicon Infiltration process (LSI). This method is based on infiltration of a porous preform made from SiC and carbon materials by the silicon melt to obtain secondary silicon carbide as a binder phase that cements the initial components into a dense material. Such technological processes are accompanied by complex physico-chemical phenomena. Understanding of these phenomena is necessary for development of optimal processes providing production of a material with required quality. Numerical simulation is a powerful tool for study and optimization of technological parameters of LSI process. In the present work, the mathematical model considers all major physico-chemical phenomena governing LSI process: flow of reactive Si melt, solid-phase diffusion of carbon and silicon atoms through the emerging SiC layer, chemical interaction between silicon and carbon, evolution of porous medium structure. In this work, we used simulations to analyse the influence of operating conditions on the LSI process and to estimate properties and quality of produced material.

CN:P04 **Effect of Surface-modified Si-Al-C® Fibre Addition on Mechanical Properties of Silicon Carbide Composite**

H. Moriyasu*, J. Kita, H. Suemasu, S. Koda, K. Itatani, Sophia University, Tokyo, Japan; I.J. Davies, Curtin University of Technology, Perth, Australia

The authors examined the effect of Si-Al-C® (SA)fibre addition on the densification and fracture toughness of silicon carbide (SiC) composite. An acid treatment (H2SO4 and HNO3) was carried out at 50 °C for 4 h in order to enhance the dispersibility of SA fibres with carbon interface in the SiC matrix, owing to the addition of COO- groups to the surface of SA fibres. Commercially available ultrafine SiC powder (specific surface area: 47.5 m2·g-1) was mixed with acid-treated SA fibre and sintering aid (4.8 mass% Al4C3 and 1.2 mass% B4C) in the presence of acetone.

Approximately 1.5 g of the mixture was uniaxially pressed at 50 MPa in order to obtain a compact with a diameter of 20 mm and a thickness of 1.5 mm. The resulting compact was hot-pressed at 1800 °C for 1 h in Ar atmosphere under a pressure of 62 MPa. The relative density of the SiC composite with no acid-treated SA fibre addition was 96.6%, whereas that of the SiC composite with acid-treated SA fibre increased to 97.7%. The former fracture toughness was 4.8 MPa·m1/2, whereas the latter fracture toughness increased to 6.5 MPa·m1/2. It is concluded from the above results that the acid-treatment of SA fibres may be effective for the densification and fracture toughness of SiC composite.

CN:P06 **Study of Tribotechnical Properties of Cf/SiC-Composites in Combination with Different Riders**

V.I. Kulik*, Baltic State Technical University, St. Petersburg, Russia; A.S. Nilov, S.E. Ryabikov, L.I. Solov’ev, Reseach-and-production company “Ceracom” Ltd, St.Petersburg, Russia; A.P. Garshin, St. Petersburg State Polytechnical University, St. Petersburg, Russia; V.V. Savich, N.A. Shipitsa, A.Ph. Ilyuschenko, A.A. Dmitrovich, Powder Metallurgy Institute, Minsk, Republic of Belarus

Cf/SiC-composites belong to the most promising advanced materials for frictional applications. An efficient way to produce frictional Cf/SiC-composites is a method of Reaction Sintering. In the present work, the production of the Cf/SiC-composite involved manufacturing of Cf-reinforced plastic preforms from chopped carbon fibres and thermosetting resin, carbonization of the preform to produce Cf-reinforced coke matrix (Cf/C-composite) with subsequent perform siliconizing by Si melt. Additionally, some samples were obtained using polymeric binder that contained powdered carbon, silicon carbide and carbon nanotubes. CMC samples were produced with varying composition. Tribotechnical parameters (friction coefficient and wear factor) were measured on the inertial stands which allow carrying out tests by scheme “plane-plane” and “plane-finger”. CMC of different compositions and frictional metalloceramics produced by a powder metallurgy method were used as fixed riders. For comparison, tests were carried out for conventional friction couple “grey iron-metalloceramics” widely used in friction units of motor transport. Tests have shown that Cf/SiC-composites in a couple with metalloceramic rider have better tribotechnical properties as compared with conventional grey iron.

HOT POSTERS

Received by May 10, 2010

CA:HP37 Sintering of High Density Ceramics Based on SiC Using Cold Hydrostatic Pressing

D.A. Kolesnikov*, O.N. Maradudina, M.G. Kovaleva, Joint Research Centre “Diagnostics of structure and properties of nanomaterials” at Belgorod State University, Belgorod, Russian Federation

High density SiC ceramics was obtained from commercially available powder with average grain size about 100 nm using reactive sintering method in convectional furnace. Mixture of amorphous boron and liquid epoxy wax in amount necessary to 3 weight percent of B_4C generation was used as an admixture relieving sintering and granulate forming. The green body was obtained using cold hydrostatic pressing. The bulk density of obtained ceramics was investigated using mercury porosimetry and hydrostatic weighing methods. SiC based ceramics obtained has 99,4% of theoretical density and 510 MPa of bending strength.

CA:HP38 Synthesis and Characterization of Al_2O_3(matrix)-30%ZrO_2 and Al_2O_3(matrix)- 30%$Y_{0.1}Zr_{0.9}O_2$ Nanocomposites

V.V. Sirota*, R.A. Lyubushkin, M.G. Kovaleva, Joint Research Centre “Diagnostics of structure and properties of nanomaterials” at Belgorod State University, Belgorod, Russian Federation

Tetragonal zirconia in alumina matrix is known as Zirconia Toughened Alumina (ZTA). ZTA ceramics are attractive materials due to the combination of both ZrO_2 (high strength and fracture toughness) and Al_2O_3(high hardness and wear resistance) properties. This work reports the synthesis of ultra-fine Al_2O_3–ZrO_2 powders (20–200 nm) through the wet chemical route. Hundred percent tetragonal ZrO_2 can be found in the sintered body Al_2O_3(matrix)-30%$Y_{0.1}Zr_{0.9}O_2$ at 1600 °C/2 h with 98% densification. The fine ZrO_2 (100-300 nm) has been homogeneously dispersed within the alumina matrix with a maximum grain size of 0.8 ìm, which will increase the toughness of the alumina matrix. High fracture toughness of Al_2O_3-30%$Y_{0.1}Zr_{0.9}O_2$ is attributed to the presence of a coupled mechanism of stress-induced transformation toughening and transformation-induced microcrack toughening, and high flexural strength of the ceramics is a coupled result of small-size flaw and high fracture toughness. Because of no amorphous phases and grain boundaries but clean and stable phase interfaces in the ceramic composite, the Al_2O_3(matrix)-30%ZrO_2 and Al_2O_3(matrix)-30%$Y_{0.1}Zr_{0.9}O_2$ obtained in the experiment are promised to have excellent strength retention and high creep resistance at high temperature, compared to ones prepared by powder sintering method.

CA:HP39 Homogeneous Nano-alloyed Ceramic Powders for Compacting

P. Lintunen*, T. Ritvonen, U. Kanerva, J. Lagerbom, T. Suhonen, T. Varis, O. Söderberg, S-P. Hannula, VTT, Advanced Materials, Tampere, Finland

Main focus of the present work is in the tailored ceramic materials and metal matrix composites with new combination of mechanical and corrosion resistance properties. The focus is on nanoalloyed ceramics so that the powder is only partially in nano range. This enables to customize composition of the powder, and to produce extremely homogeneous structure with lower cost and better processability when compared to fully nanostructured powders. Homogeneous dispersions from ceramic-ceramic-composites or ceramic-metal-composites were processed by novel powder processing equipments mainly in water-based solutions. These nanoalloyed ceramic powders were further processed into coatings by a new thermal spray system Carbide Jet Spray (CJS) or into components by Spark Plasma Sintering (SPS).

CB:HP27 Spark Plasma Sintering of Boron Carbide and Effects of Various Additives on Sintering and Material Properties

Yusuf Celik*, Gultekin Goller, Onuralp Yucel, Filiz Sahin Filiz Sahin, Istanbul Technical Universty, Metallurgical And Material Engineering, Istanbul, Turkey

In this study, it was aimed to produce dense and mechanically strong boron carbide ceramics by using some oxide additives. Physical properties of two different grades pure boron carbide powders were analysed and then sintered by Spark Plasma Sintering Method. Starting powders were prepared by ball milling with addition of 5 weight % Y2O3, Al2O3, SiO2 and Y2O3 + Al2O3 respectively.In the sintering step powder mixtures were sintered by SPS sintering method in round-shaped graphite dies under 50 Mpa for 5 minutes in the range of 1700-1800 °C. In the characterization step ,sintered specimens were characterized by XRD and SEM techniques. The hardness values were measured under 1000 g load and the density values were measured with Archimedes' principle. The 3-point bending and fracture toughness analysis were also conducted.

CE:HP17 Silicon Carbonitride/Zirconia Ceramic Nanocomposites - Synthesis and High Temperature Behavior

C. Linck*, E. Ionescu, H.-J. Kleebe, R. Riedel, Technische Universität Darmstadt, Institut für Materialwissenschaft, Darmstadt, Germany

Polymer-derived SiCN/ZrO2 ceramic nanocomposites have been prepared via chemical modification of a commercially available polysilazane with Zr(OnPr)4 as zirconia precursor. The prepared materials were subsequently cross linked and pyrolyzed at 1100 °C in argon atmosphere to provide SiCN/ZrO2 ceramic nanocomposites. The cross-linking and ceramization processes have been investigated by thermogravimetric analysis (TGA) coupled with in-situ mass spectrometry (MS) and FTIR spectroscopy. The obtained SiCN/ZrO2 materials were characterized via powder XRD, elemental analysis, Raman spectroscopy as well as electron microscopy (SEM, TEM). In order to assess the thermal stability of the prepared nanocomposites towards decomposition, annealing experiments at temperatures from 1400° to 1600°C were performed under argon and nitrogen atmosphere. The annealed samples were investigated with respect to chemical and crystalline phase composition as well as to microstructure evolution. The high temperature behavior of the prepared ceramics will be presented and discussed in the light of the thermal behavior of zirconia-free SiCN ceramics.

CE:HP18 Control of Electrical Conductivity of CNT Dispersed Si3N4 Ceramics by Double Percolation

S. Yoshio*, J. Tatami , T. Wakihara, T. Yamakawa, K. Komeya, T. Meguro, Yokohama National University, Graduate school of Environment and Information Sciences, Yokohama, Kanagawa, Japan

The purpose of this study is to control electrical conductivity of carbon nanotubes (CNTs) dispersed Si3N4 ceramics by double percolation. We prepared two kind of CNT dispersed Si3N4 ceramics. Double percolation sample was prepared using the mixed granules with various amounts of CNTs (1.0～3.0wt%) and without CNTs in the proportion of 50 to 50. The powder mixtures were sintered by spark plasma sintering technique to obtain fully dense CNT dispersed Si3N4 ceramics. For comparison, single percolation sample with various amounts of CNTs (0.5～3.0wt%) were also prepared in the similar condition. The relative density of the sintered bodies was over 97%. The single percolation sample having 0.5wt% CNT did not show electrical conduction because the amount of CNT was fewer than the percolation threshold. On the other hand, the electrical conductivity of double percolation sample having 0.5wt% CNT was about five orders of magnitude more than that of 0.5wt% single percolation sample and it also increased with an increase in applied electric field. Consequently, it was shown that the electrical conductivity of CNT dispersed Si3N4 was able to be controlled by double percolation.

CE:HP19 The Influence of Microstructure on Mechanical Properties of Cr_3C_2-TiC Composites

G. Grabowski, AGH - University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Advanced Ceramics, Cracow, Poland

Carbides of transition elements groups shows very high hardness and high melting temperatures. However their wider use as constructional materials is limited by their moderate toughness. The Ti-Cr-C system, examined in the work, has limited mutual solubility, that allows to make synthesis of composite materials. Moreover the addition of chromium carbide shows very positive influence on microstructure and properties of particular composites of titanium carbide. The modifier decreases the sintering temperature, limits the grain growth of TiC and essentially improves toughness. The commercial powders of TiC and Cr_3C_2 were used in the work to manufacture composites. Four compositions, containing from 10 to 75 mol% of Cr_3C_2 were selected on the base of analysis of phase equilibrium diagram. The materials were sintered using hot pressing. Phase analysis, microstructural observations, and basic mechanical properties were made.

The work was financially supported by grant of the Ministry of Science and Higher Education (N N507 451034)

CF:HP24 Photocatalytic Reduction of Nitrogen Oxides to Dinitrogen in Aqueous Suspension of Metal-loaded Titanium(IV) Oxide

Hiroshi Kominami*, Hitoshi Gekko, Yumiko Shimada, Keiji Hashimoto, Department of Applied Chemistry, Kinki University, Higashiosaka, Osaka, Japan

Nitrite (NO2-) and nitrate (NO3-) in water and gaseous NOx are toxic species to a human body. A purpose of this study is to show that NO3- and NOx are photo-catalytically reduced to N2 under the same conditions. Degussa P25 TiO2 powders were used as received. Photodeposition method was used to prepare metal Pd(1 wt%)-Ag (4 wt%)-TiO2. Sodium nitrite or NOx was added to aqueous suspensions of Ag-Pd-TiO2 in the presence of sodium oxalate (OA) (200 µmol) as hole scavenger. The suspension was irradiated with a 400 W high-pressure mercury arc (>300 nm) with magnetic stirring under argon at 298 K. Amounts of evolved hydrogen (H2), NOx and N2 were measured with gas chromatograph. NO3- and NO2- in the liquid phase were measured with ion chromatograph. In the photocatalytic reduction of NO3- in aqueous suspension of Pd-Ag-TiO2, the amount of NO3- decreased with irradiation time, whereas the amount of N2 was increased. NO3- was almost completely converted to N2 after 24 h. Selective photocatalytic reduction of N2O to N2 was also investigated under the same conditions. The amount of N2O decreased with irradiation time whereas the amount of N2 was increased and N2O was almost completely converted to N2 after 3 h. Photocatalytic reduction of other NOx to N2 was also confirmed.

CH:HP28 Diffuse Phase Transition and Ferroelectric Properties of Ceramic Solid Solutions in New $SrTiO_3$-$BiScO_3$ System

O.N. Ivanov*, E.P. Danshina, Joint Research Centre "Diagnostics of structure and properties of nanomaterials" at Belgorod State University, Belgorod, Russian Federation

Ceramic solid solutions of (1-x)$SrTiO_3$-(x)$BiScO_3$ system with x=0, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 have been for the first time synthesized via solid-state processing techniques. Both of end compounds in this system are not ferroelectric materials. X-ray diffraction analysis revealed that at room temperature the samples under study at x=0.2, 0.3, 0.4 and 0.5 consist of mixture of center-symmetric cubic Pm3m phase and polar tetragonal P4mm phase. Anomalous behavior of dielectric permittivity and dielectric losses for these samples is found to be specific one for ferroelectrics with diffuse phase transitions. It was found that the degree of diffuseness of phase transition is increasing with increasing $BiScO_3$ content. This can be explained by the increased cation disorder due to the substitution on the A-site by Bi and on B-site by Sc. Examination of the polarization hysteresis behavior revealed nonlinear hysteresis loop that can be taken as additional evidence for ferroelectrcity of the samples under study.

CH-6:HP11 The Interplay of Coupled Charge, Spin and Structure in the Presence of Dynamics in Magnetoelectric $EuTiO_3$

L.J. Spalek*[1, 2], S.E. Rowley[2], M. Shimuta[3], T. Katsufuji[3], O. Petrenko[4], C. Mazzoli[5], V. Scagnoli[5], H. Walker[5], M. Allietta[6], M. Scavini[6], S.S. Saxena[2], C. Panagopoulos[1-7], [1]Institute of Electronic Structure and Laser, FORTH, Greece; [2]Cavendish Laboratory, University of Cambridge, UK; [3]Department of Physics, Waseda University, Japan; [4]Department of Physics, University of Warwick, UK; [5]ESRF, France; [6]Department of Physical Chemistry, University of Milan, Italy; [7]Department of Physics, University of Crete, Greece

The interplay of coupled spin, charge and structural degrees of freedom in the presence of dynamics is known to lead to novel complex phases. Here we present the case of magnetoelectric $EuTiO_3$, a Rare-Earth transition metal oxide perovskite. The system is cubic with a lattice constant of 3.9A at room temperature. At temperatures of 150K<T<300K we observe an onset of a previously unreported cubic to tetragonal structural phase transition which locks in below T=50K[1]. At T~80K we provide evidence for the onset of charge dynamics in accord with corresponding features in the magnetic susceptibility. Consequently, we may expect a connection between the three subsystems. Indeed, there is an identifiable temperature length-scale, T~80K, which most likely results in unusual low temperature phases. These include unusual antiferromagnetism[2], magnetoelectric coupling[3] and a new low temperature magnetic phase. The correspondence between dynamics and the resulting complex phases may promote the appearance of low temperature (anti)ferroelectricity reflecting its intrinsically dynamic origin

[1]Allieta M. et al, (in preparation); [2]T.R. McGuire, M.W. Shafer, R.J. Joenk, H.A. Alperin, S.J. Pickart, J.Appl. Phys., 37: 981 (1966) and references therein; [3]T. Katsufuji, H. Takagi, Phys. Rev. B, 64: 054415 (2001).

CH-6:HP12 Synthesis, Characterization, and Magnetic Properties of Multiferroic Chromates

Anna Pimenov*[1], P. Mandal[2], V. Tsurkan[1], M. Hemmida[1], F. Mayr[1], H.-A. Krug von Nidda[1], A.Loidl[1], [1]Experimentalphysik V, EKM, University of Augsburg, Augsburg, Germany; [2]Saha Institute of Nuclear Physics, Calcutta, India

Multiferroic properties have been reported recently in several ACrO2 delafossite and LnCrO3 perovskites[1, 2, 3]. The former compounds are two-dimensional triangular lattice antiferromagnets with helical spin structures in the long-range ordered phase. The latter ones are three dimensional spin systems with complex magnetic order. To study the microscopic mechanism of multiferroicity it is necessary to guarantee high-quality samples of exact stoichiometry. We describe the preparation routes for the series of ACrO2 (A= Cu, Ag, Li, Pd) and LnCrO3 (Ln=Y,La,Eu,Tb,Er,Yb,Lu) chromates using solid-state reaction technique at different temperatures and partly using a two-stage substitution procedure. We describe the preparation routes for these samples and discuss their structural and magnetic properties. In addition a single crystal of CuCrO2 has been grown by flux method.

[1]S. Seki et al, Phys. Rev. Lett. 101, 067204 (2008; [2]H. Takatsu et al, Phys. Rev. B 79, 104424 (2009; [3]H.B. Lal et al, J. Mater. Sci. Lett. 14, 9 (1995).

CJ:HP22 Investigation of Usage of Clay with Rheological Difficulties in Wall Tile

Baran Tarhan[1, 2]*, Nuran Ay[1], Celal Yildiz[2], [1]Anadolu University, Material Science and Engineering Department, Eskisehir, Turkey; [2]Seramiksan Turgutlu Seramik San.ve Tic.A.S., Manisa, Turkey

Traditional tile production made by wet milling. Tile recipes consist of large amount of clays. Some local clays which are used in tile production cause rheological problems with traditional wet milling process. With dry milling amount of local clays can be increased. Effects of dry grinding on wall tile composition are investigated with experimental design method. Experiments were designed as $2^4 3^1$ multi-level factorial design, individual effects of main five factors (temperature, Turgutlu clay, sandy clay, Istanbul clay and Na-feldspar) and their interactions were determined. 24 formulations are prepared with territorial clays (Turgutlu/Manisa/Turkiye region) and feldspar. The samples were ground at laboratory hammer mill and unidirectional dry pressed in a die with rectangular cavity (5 cm x 10 cm).The samples were fired at 1100 and 1135 °C using a fast firing cycle in a laboratory roller kiln. The samples were characterized before and after firing by using XRD, and SEM. The physical properties (linear shrinkage, flexural strength and water absorption) were measured. Results were analyzed by MINITAB 14 statistical software program. With dry milling rheological problems can be eliminated and it is possible to use these types of clays in wall tile. The experimental results showed that it was possible to obtain a dry ground wall tile body with the properties in accordance with ISO-EN 10545.

CJ:HP23 The Investigation of Glassy Phase Compositions for Porcelain Tile Bodies

Muge Tarhan[1]*, Ferhat Kara[2], Figen Aydin Egri[3], [1]Kutahya Seramik, Kutahya, Turkey; [2]Anadolu University, Department of Materials Science and Engineering, Eskisehir, Turkey; [3]Yurtbay Seramik, Eskisehir, Turkey

The sintering of porcelain tiles undergoes by viscous flow sintering. The rate of viscous flow sintering in a porcelain body is controlled by viscosity of the glassy phase. The aim of the present study is to investigate the relationship between compositional-thermal behavior of glassy phase formulations in order to lower sintering temperatures and/or firing cycles of porcelain stoneware tiles. Glassy phase composition of a standard porcelain tile was determined by some assumptions based on literature review and was taken as a reference. Alkali and earth alkali ratios, alumina and silica content were all modified in a systematic manner. Modifications of the glassy phase composition were made by using Seger formula. Hot stage microscopy was used to analyze thermal behavior of the glassy phases and glassy phase composition with lowest softening point. The glass transition temperature (T_g) of the glassy phases were determined by a dilatometer. The glassy phase viscosities were calculated employing HSM data in the association with T_g values obtained from dilatometer.

CJ:HP24 Using Ultrasonic Test Method in Characterization of Physical and Mechanical Properties of Porcelain Tile

Elif Eren*, Semra Kurama, Anadolu University, Department of Materials Science and Engineering, Eskisehir, Turkey

Ultrasound affords very useful and versatile non-destructive method, using in very large application area for evaluating the microstructure and mechanical properties of materials. In this study, porcelain tiles were sintered at different temperatures to change their porosity, after that the time of flight of longitudinal and shear waves was measured trough the tile. Time of flight of ultrasonic waves was measured by using a contact ultrasonic transducer operating on pulse-echo mode. Using the time of flight of ultrasonic wave and thickness of tiles, the velocity of the waves and dynamic Young’s modules were determined. To calculate firing strength and static Young’s modulus of the tiles three point bending test analyse was used. Results were discussed by comparing of changing in velocity with firing strength. Additionally the two methods, using in measuring of Young’s modules, were compared.

CJ:HP25 Using High Power Diode Laser for Repairing Sanitary-Ware Ceramics Surface Imperfections

Evren Baskut*, Aydin Dogan, Anadolu University, Department of Materials Science and Engineering, Eskisehir, Turkey

Ceramic sector is one of the most energy consuming sector in the world. Imperfections on ceramic surface which occurs after gloss firing process have to be re-fired for the quality standards. Therefore we aimed to develop the fast and economical technique by using high power diode laser (HPDL) and specially developed low melting white-opaque frit towards the localized heat-treating of surface imperfections by eliminating further firing step. Artificially made 2 mm diameter 3 mm depth holes on glazed surface by 60 w 1064 nm Nd-YAG laser and have been filled with specially developed low melting white-opaque frit then irradiated by 300 w, 810 nm (CW) high power diode laser (HPDL). The samples were then examined using optical microscopy, scanning electron microscopy (SEM) and energy disperse X-ray analysis (EDX) techniques. The work clearly shows that localized heat-treating of sanitary ware ceramics surface without micro cracks and porosities can be possible with using high power diode lasers.

CJ:HP26 Kinetic Study on Controlled Crystallization of a Ca2ZnSi2O7 Phase in Materials Obtained from Vitrification of Metallurgical Slag and Recycled Soda Lime Glass

E.I. Cedillo González*[1], J.J. Ruiz Valdés[1, 2], A. Álvarez Méndez[1], [1]Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Monterrey, N.L. México; [2]Centro de Innovación, Investigación y Desarrollo en Ingeniería y Tecnología CIIDIT, Universidad Autónoma de Nuevo León, Apodaca, N.L., México

Non isothermal kinetics of a glass obtained from a mixture of 59 wt % of metallurgical slag and 41 wt% of soda lime recycled glass was studied by differential thermal analysis (DTA), x-ray diffraction (XRD) and scanning electron microscopy (SEM). The curves of differential thermal analysis revealed the presence of two exothermic peaks, a major peak at 810 °C and a minor peak at 1085 °C. DRX revealed that the first exothermic peak corresponds to the formation of hardystonite, Ca2ZnSi2O7 and aegirine, NaFe3+Si2O6, while the second minor peak corresponds to the formation of zinc ferrite, ZnFe2O4. The activation energy of the crystallization, Ea, was calculated with the Kissinger equation from DTA data, obtained at different heating rates. In addition, the particle size effect on the kinetics of crystallization was studied. The Avrami factor, n, was calculated with Augis-Bennett method. The value of obtained Ea increase with bigger particle sizes and also the value of n, indicating that for small particles the superficial crystallization mechanism is predominant, while bulk mechanism is preferential on large particles. Obtained materials are suitable for some structural applications.

CJ:HP27 Reducing Pyroplastic Deformation of Sanitaryware Porcelain Bodies

Derya Yesim Tunçel[1]*, Mustafa Kerim Kara[2], Emel Özel[3], [1]Anadolu University, Graduate School of Sciences, Ceramic Enginnering Department, Eskisehir, Turkey; [2]Duravit Yapý Ürünleri San. ve Tic. A.ª., Organize Deri Sanayi Bölgesi, Tuzla,Ýstanbul; [3]Anadolu University, Department of Materials Science & Engineering, Eskisehir, Turkey

Pyroplastic deformation is the bending of a ceramic specimen caused by gravity during heat treatment and especially, in large bodies of sanitary wares, is not only an economical problem during the production process but brings about limitations to design of large sanitary ware products as well. For this reason, this study aims at reducing pyroplastic deformation of sanitary ware porcelain by means of size reduction of non-plastic raw materials of standard composition and also by designing a new composition. Three different porcelain bodies, standard body S1 and the two porcelain bodies which have lower average particle size than standard, S2 and S3 were prepared. After attemps of composition design a new composition coded “SK” was produced using Seger formula approach to reduce pyroplastic deformation of the standard composition. Pyroplastic deformation behavior of bodies within a controlled firing regime was investigated by using fleximeter. X-ray diffraction (XRD) was used to analyze the phases formed after firing. Scanning electron microscopy (SEM) was employed to observe microstructural characteristics of the fired bodies. The pyroplastic deformation values of bodies were also measured on the specimens which have a special shape to deform during firing. The results of particle size reduction in order to reduce the firing temperature of the standard composition showed that the appropriate firing temperature was lowered from 1250 to 1210 causing the expected deformation reduction from 40 mm to 36 mm. The composition “SK” has a firing temperature of 1240 and has a deformation value of 27 mm, which is 33% lower than standard body.

CL:HP05 Alumina-Mullite Refractories: Prototypal Components Production for Thermal Shock Tests

A. Brentari*, M. Labanti, F. Mazzanti, C. Mingazzini, S. Sangiorgi, M. Villa, ENEA, Engineering of Components and Processes Section, Faenza Research Centre, Faenza, Italy; S. Martelli, D. Olevano, Centro Sviluppo Materiali S.p.A., Rome, Italy

Alumina-mullite refractory tiles are used as liners in gas turbines for power production, for the thermal insulation of the combustion chambers. The typical microstructure is characterized by a coarse fraction, in order to increase porosity (and hence thermal insulation) and improve thermal shock resistance (by grain bridging mechanism). A mixture of alumina and ceramic wastes (Al_2O_3 45%, SiO_2 55%) was optimized to manufacture prototypal components, by cold isostatic press (CIP). On sintering at 1600 °C, a final composition of 40% mullite and 60% alumina was obtained. For the productions of refractory tiles with dimensions similar to the commercial ones, an appropriate mould was CAD-CAM designed and produced, using aluminium and silicone. 115 x 95 x 30 mm^3 tiles were obtained and utilized for thermal shock tests. Samples were heated up to 1000 °C and quenched to 20 °C: this cycle was repeated 30 times before inspecting the macroscopic cracks. The results were compared with those obtained with a standard test for advanced technical ceramics based on MOR measurements (EN 820-3, Determination of resistance to thermal shock by water quenching). Two different pressing conditions were tested (60 and 150 MPa) in order to get data about a possible industrial production by uniaxial pressing.

CL:HP06 New Materials for Ceramic Tile Bodies

Gülfem Bynal*, Nuran Ay, Anadolu University, Department of Materials Science and Engineering, Eskisehir, Turkey

The magnesite deposits of Tutluca village (W of Eskisehir) lie in serpentinized harzburgites and dunites of Alpine type ultramafic rocks. Magnesite mineralization within these rocks forms individual veins and stockwork type magnesite in fractures and cracks. These rocks are treated to an enrichment process in order to obtain pure magnesite. Chemical and physical properties of the residual samples taken from this enrichment process show that they are promising batch mineral for manufacturing ceramic materials. In the present work the possibility of using these samples, to make ceramic tile is explored. For this purpose the features of the materials were investigated by applying physical, mechanical, thermal analysis, x-ray diffraction at different temperatures and x-ray fluorescence spectroscopy. X-ray diffraction analysis showed that main crystal of these rocks is orthochrysotile which is one of serpentine polymorphs. As a result of this study, it has been seen that the samples can be used as alternative raw materials for ceramic tile bodies such as marble and feldspar.

CL:HP07 Examination of Microstructural Characteristics and Mechanical Properties of MgO-$MgAl_2O_4$ Composite Refractories with the Addition of ZrO_2-Y_2O_3

Tuba Aksoy*, Cemail Aksel, Anadolu University, Department of Materials Science and Engineering, Eskisehir, Turkey

The incorporation of spinel particles into MgO improves thermal shock resistance and thereby service life of refractories. However, mechanical properties of MgO-spinel refractories are quite low. Therefore, the effect of spinel and ZrO_2-Y_2O_3 additions at different ratios has been examined to improve mechanical properties of MgO-spinel composites in this work. The relationships between mechanical properties and microstructural variables have been investigated in detail. The inclusion of ZrO_2-Y_2O_3 particles into MgO-spinel composites increased the mechanical properties significantly. The important parameters improving the mechanical properties of MgO-Spinel-(ZrO_2-Y_2O_3) composite refractory materials have been determined as follows: i) as the microcracks formed in the structure come across either with the additives or pores; crack branching and deviation of interlinking microcrack network or crack arresting occur, ii) the trend of fracture type has been converted from transgranular to intergranular fracture with increasing amount of additives, iii) as the additive content increases, grain size of MgO decreases significantly, as compared to pure MgO material, iv) the density values and critical crack length increase with increasing amount of additives. Thermal shock parameter R_{st} has determined that the materials incorporated ZrO_2-Y_2O_3 show a marked increase in thermal shock resistance and thus they will show a long-life performance in service for high temperature applications.

CM:HP09 Nanotoxicity of CdTe quantum dots

Yuanyuan Su, Mei Hu, Chunhai Fan, Yao He, Qingnuan Li, Wenxin Li, Qing Huang*, Shanghai Institute of Applied Physics, CAS, Shanghai, China

In this report, we evaluated the cytotoxicity of a series of quantum dots (QDs) directly synthesized in aqueous phase, i.e., thiols-stabilized CdTe, CdTe/CdS core-shell structured and CdTe/CdS/ZnS core-shell-shell structured QDs, with a variety of cell lines including K562 and HEK 293T. We have demonstrated that the CdTe QDs are highly toxic for cells due to the release of cadmium ions. Epitaxial growth of a CdS layer reduces the cytotoxicity of QDs to a small extent. However, the presence of a ZnS outlayer greatly improves the biocompatibility of QDs, with no observed cytotoxicity even at very high concentration and long-time exposure in cells. A systematic study on the relationship of the cytotoxicity of quantum dots (QDs) and the free cadmium ions released from them was also carried out, using CdCl2 solution as control with known amounts of Cd2+. The results showed that the CdTe QDs were severer cytotoxic than CdCl2 solutions when the intracellular Cd2+ concentrations were identical in HEK293 cells treated with them, implying that the cytotoxicity of CdTe QDs cannot attributed solely to the toxic effect of free Cd2+.