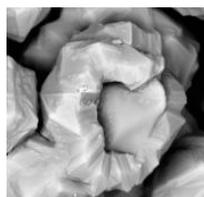


3rd International Conference on Competitive Materials and
Technology Processes

Miskolc-Lillafüred, Hungary
October 6-10, 2014

BOOK OF ABSTRACTS

Edited by
László A. GÖMZE



ic-cmtp3

Copyright C2014 by IGREX Engineering Service Ltd.

All rights reserved. No part of this publication must be reproduced without a written permission from the copyright holder.

3rd International Conference on Competitive Materials and Technology Processes
Book of Abstracts
Miskolc-Lillafüred, Hungary
October 6-10, 2014
Edited by: Prof. Dr. László A. GÖMZE

Citation of abstracts in this volume should be cited as follows:
<Author> (2014) <Title>. In L.A. Gömze (Editor) 3rd International Conference on Competitive Materials and Technology Processes, Miskolc-Lillafüred, Hungary, pp.

ISBN 978-963-12-0334-9

Published in Hungary – Igrax Ltd. Igrici, Hungary
Printed in Hungary – Passzer 2000 Ltd, Miskolc, Hungary

ORGANIZED BY

Organized by the International Scientific Advisory Board (**ISAB**), by the International Organization Board (**IOB**) and by the Session and Symposium chairs.

THE INTERNATIONAL SCIENTIFIC ADVISORY BOARD (ISAB)

Dr. Priscila ANADÁO, University of São Paulo (Brasil)

Dr. Raffaella DEMICHELIS, Curtin University (Australia)

Prof. Dr. Cheng-Ji DENG, Wuhan University of Sci and Tech. (China)

Prof. Dr. Katherine T. FABER, Northwestern University (USA)

Prof. Dr. Saverio FIORE, CNR Institute of Methodologies (Italy)

Prof. Dr. László A. GÖMZE, University of Miskolc, (Hungary)

Prof. Dr. Kiyoshi ITATANI, Sophia University (Japan)

Prof. Dr. Sergey N. KULKOV, Tomsk State University (Russia)

Prof. Dr. John M. PARKER, The University of Sheffield (UK)

Prof. Dr. Tohru SEKINO, The University of Osaka (Japan)

Prof. Dr. David S. SMITH, University of Limoges (France)

Prof. Dr. Bojja SREEDHAR, CSIR-Indian Institute of Chemical Technology (India)

THE INTERNATIONAL ORGANIZATION BOARD (IOB)

Dr. Priscila ANADÁO, University of São Paulo (Brasil)

Prof. Dr. Dong Sik BAE, Changwon National University (Korea)

Dr. Fares BEAINY, Volvo Construction Equipment (USA)

Prof. Dr. Philippe BLANCHART, ENSCI Limoges University (France)

Dr. Adorján BOROSNYÓI, Technical University of Budapest (Hungary)

Prof. Dr. Saveiro FIORE, National Research Council (Italy)

Prof. Dr. Elzbieta GODLEWSKA, AGH University (Poland)

Dr. Ludmila N. GÖMZE, Igrex Ltd. (Hungary)

Prof. Dr. Olga KOTOVA, RAS Institute of Geology (Russia)

Prof. Dr. Hiromitsu KOZUKA, Kansai University (Japan)

Prof. Dr. Sergey N. KULKOV, Tomsk State University (Russia)

Prof. Dr. Huey-Jinan LIN, National United University (Taiwan)

Prof. Dr. Vasily LUTSYK, Buryat State University (Russia)

Prof. Dr. Líviu MARSAVINA, Polytechnic University of Timisoara (Romania)

Prof. Dr. Fujio MIZUKAMI, National Institute AIST (Japan)

Dr. Güntner MOTZ, University of Bayreuth (Germany)
Prof. Dr. John M. PARKER, The University of Sheffield (UK)
Prof. Dr. Tomasz SADOWSKI, Lublin University of Technology (Poland)
Prof. Dr. Tsugio SATO, Tohoku University Sendai (Japan)
Prof. Dr. Michael SCHEFFLER, Otto-von-Guerike University (Germany)
Prof. Dr. Igor SHABALIN, The University of Slaford (UK)
Prof. Dr. Bojja SREEDHAR, CSIR-Indian Institute of Chemical Technology (India)
Prof. Dr. Jean-Claude TEDENAC, University of Montpellier 2 (France)
Dr. Nicolas TESSIER-DOYEN, ENSCI, Limognes University (France)
Md. Prof. Alexandr L. URAKOV, Izhevsk State Medical Academy (Russia)
Dr. Hao WANG, Wuhan University of Science and Technology (China)

THE ORGANIZER SESSION CHAIRS AND SYMPOSIUM CHAIRS

Session 1. Advanced Materials for Bio- and Medical Applications

MD. Prof. Dr. Alexandr L. URAKOV, (Russia)

Session 2. Advanced Materials for Extreme Applications

Dr. Ludmila N. GÖMZE, (Hungary)

Session 3. Advanced Nanomaterials with Predesigned Properties

Prof. Dr. Elzbieta GODLEWSKA, (Poland)

Session 4. Bioaterials Derived Ceramics and Composites

Prof. Dr. Bojja SREEDHAR, (India)

Session 5. Glasses, Coatings and Related Materials

Prof. Dr. Nikolay NIKONOROV, (Russia)

Session 6. Hetero-Modulus and Hybrid Materials

Prof. Dr. Tohru SEKINO, (Japan)

Session 7. Light-Weight Metals and Alloys

Prof. Dr. Jean-Marie DREZET, (Switzerland)

Session 8. Materials with Extreme Dynamic Strength

Prof. Dr. László A. GÖMZE, (Hungary)

Session 9. Membranes and Catalysts

Dr. Priscila ANADÁO, (Brasil)

Session 10. Minerals for Environmental and Medical Application

Prof. Dr. Saveiro FIORE, (Italy) and Prof. Dr. Olga KOTOVA (Russia)

Session 11. Nanomaterials for Environment and Health

Prof. Dr. Tsugio SATO, (Japan)

Session 12. Novel Synthesis and Processing Technology

Prof. Dr. Sergey N. KULKOV, (Russia)

Session 13. Phase Diagram as a Tool of Materials Science

Prof. Dr. Vasily LUTSYK, (Russia) and Prof. Dr. Jean-Claude TEDENAC, (France)

Session 14. Polymer Derived Ceramics

Prof. Dr. Michael SCHEFFLER, (Germany)

Session 15. Processing and Properties of Silicate Ceramics

Dr. Nicolas TESSIER-DOYEN, (France)

Session 16. Testing and Characterization of Materials – Methods, Equip. and Errors

Dr. István Kocserha, (Hungary)

is-icbm1. The 1st International Symposium on Innovative Carbon Based Materials

Prof. Dr. Igor L. SHABALIN, (United Kingdom) and Dr. Hao WANG (China)

is-icm1. The 1st International Symposium on Innovative Construction Materials

Prof. Dr. Tomasz SADOWSKI (Poland), Dr. Adorján BOROSNYÓI (Hungary),

Prof. Dr. Líviu MARSAVINA (Romania) and Prof. Dr. László A. GÖMZE (Hungary)

ACKNOWLEDGEMENT

In the name of ic-cmtp3 Conference Board I would like acknowledge and say many thanks to our following sponsors for their support in press-campaign and contributions in their media:

AIPEA – International Association for the Study of Clays

Applied Rheology – International Sci. Journal on Rheology (Switzerland)

biomat.net – The Biomaterials Network (Portugal)

cfi – ceramic forum international (Germany)

ECA – European Crystallographic Association

ESR – The European Society of Rheology

építőanyag – Journal of Silicate Based Composite Materials (Hungary)

GFC – Groupe Francais de la Céramique (France)

ICG – International Commission of Glass

Igrex Ltd. (Hungary)

KSSS - The Korean Society of Spine Surgery (KOREA)

Landes Biosciences (USA)

ME – Miskolci Egyetem / University of Miskolc (Hungary)

refractory WORLDFORUM – Scientific Journal (Germany)

RAS – The Russian Academy of Sciences

SB-RAS Institute of Strength Physics and Materials Science (Russia)

SBAO – Society for Biomaterials and Artificial Organs (India)

SZTE – Scientific Society of Silicate Materials (Hungary)

TSU – Tomsk State University (Russia)

Many thanks to colleagues of **ISAB**, **IOB** and to session and symposium chairs for their support and help in organization work and in successful transaction of the 3rd International Conference on Competitive Materials and Technology Processes (**ic-cmtp3**).

I would like to say many thank personally to Prof. Dr. Tohru Sekino (The University of Osaka), Prof. Dr. Sergey N. Kulkov (Tomsk State University), Prof. Dr. Tomasz SADOWSKI (Lublin University of Technology), Md. Prof. Alexandr L. URAKOV, (Izhevsk State Medical Academy), Prof. Dr. Jean-Claude TEDENAC, (University of Montpellier 2), Prof. Dr. Bojja SREEDHAR (Indian Institute of Chemical Technology), and to Jean-Marie DREZET (Ecole Polytechnique Federale Lausanne) for their excellent organization works in Japan, Russia, Asia and European Union. Especially many thanks to Prof Dr. Olga KOTOVA and to Dipl. Ing. Rosemary Vocht-Mields for their strong support in scientific public life as wel as in press and media.

Prof. Dr. László A. Gömze
chair of conference board

PREFACE

The competitiveness is one of the most important component of our life and it plays key role in efficiency both of organizations and societies. The more scientific supported and prepared organizations develop more competitive materials with better physical, mechanical, chemical and biological properties and the leading companies are applying more competitive equipment and technology processes. The aims the 3rd International Conference on Competitive Materials and Technology Processes (**ic-cmtp3**) and the parallel organized symposiums of **is-icbm1** and **is-icm1** are the followings:

- Promote new methods and results of scientific research in the fields of material, biological, environmental and technology sciences;
- Change information between the theoretical and applied sciences as well as technical and technological implantations.
- Promote the communication between the scientist of different nations, countries and continents.

Among the major fields of interest are innovative materials with increased physical, chemical, biological, medical, thermal, mechanical properties and dynamic strength; including their crystalline and nano-structures, phase transformations as well as methods of their technological processes, tests and measurements. Multidisciplinary applications of material science and technological problems encountered in sectors like ceramics, glasses, thin films, aerospace, automotive and marine industry, electronics, energy, construction materials, medicine, biosciences and environmental sciences are of particular interest.

In accordance to the program of the conference **ic-cmtp2**, and Symposiums **is-icbm1** and **is-icm1** more than **350** inquires and registrations from different organizations were received. Finally more than **240** abstracts were accepted for presentation. From them **12** are PLENARY lectures, and **112** ORAL presentation. Scientists and researchers have arrived to Miskolc-Lillafüred (Hungary) from **41** countries of Asia, Europe, Africa, North and South America.

In this book are presented abstracts from more than **700** authors and co-authors.

Prof. Dr. László A. Gömze
chair, ic-cmtp3

CONTENTS

Plenary lectures	9
Session 1. Advanced Materials for Bio- and Medical Applications	21
Session 2. Advanced Materials for Extreme Applications	48
Session 3. Advanced Nanomaterials with Predesigned Properties	73
Session 4. Biomaterials Derived Ceramics and Composites	84
Session 5. Glasses, Coatings and Related Materials	94
Session 6. Hetero-Modulus and Hybrid Materials	111
Session 7. Light-Weight Metals and Alloys	120
Session 9. Membranes and Catalysts	129
Session 10. Minerals for Environmental and Medical Application	138
Session 11. Nanomaterials for Environment and Health	149
Session 12. Novel Synthesis and Processing Technology	161
Session 13. Phase Diagram as a Tool of Materials Science	189
Session 14. Polymer Derived Ceramics	202
Session 15. Processing and Properties of Silicate Ceramics	210
Session 16. Testing and Characterization of Materials – Methods, Equipment and Errors	219
is-icm1. The 1st International Symposium on Innovative Construction Materials	241
is-icbm1. The 1st International Symposium on Innovative Carbon Based Materials	267

Development of new materials and structures based on managed physico-chemical factors of local interaction

Aleksandr Urakov
urakoval@live.ru

Department of Pharmacology, Izhevsk State Medical Academy, 426034 Izhevsk, Russia

Conducted a study of the dynamics of local temperature, light, acidity, alkalinity, osmotic pressure, the saturation of gases and some other physical and chemical factors of local interaction products of medical purpose (surgical instruments, dental, gynecological, the funds readjustment, devices and means of hygiene, sanitation and care) and medicines (tablets, solutions for injections, ointments and creams) with the skin, subcutaneous fatty tissue, subcutaneous veins, with liquid blood, blood clots, with the contents of the stomach, intestines, sinus passages with pancreatonecrosis, osteomyelitis, with biliary stones, sulfur tubes, tearful stones, with a thick and liquid pus from different sections of the body of patients with mucous membranes of the organs of vision, sinuses, stomach, nose, external ear canal, pleural and peritoneal cavities of the body of adults and infants, as well as experimental animals in norm, pathology and treatment. It is shown that there is stability, and a significant variability of physical and chemical characteristics, on the one hand, biological objects, on the other hand, medical and pharmaceutical products. However, to date, no systematic presentation about when, why and in what permissible range of the need to artificially modify certain physical and chemical characteristics of both a medical and/or pharmaceutical products as a biological object, with whom they come in contact or in which they are be entered.

In particular, by manufacture of tablets is not taken into account compliance of condition of tissues in gastrointestinal tract of the patient with the introduction through the mouth, through a tube or through the rectum such physical and chemical characteristics of these products, as shape, size, weight, gravity, hardness, solubility, acidity, osmotic pressure in, the presence of water and gases. Therefore, modern tablets are not natural form, size, hardness, density, acidity and other physical and chemical characteristics. Therefore, when chewing of modern tablets they break the teeth, dental fillings, crowns, braces and other dental design, and cause chemical burns of the enamel and the mucous membranes of gastrointestinal tract. Therefore, all the tablets are drowning in gastric juice, fall to the bottom of the stomach, where cause an ulcer pyloric. On the other hand, in the production of gastrical, intestinal and other probes, urological, intravascular catheters, respiratory masks, intubation tubes and other medical instruments not considered «right» change their physical and chemical characteristics with the introduction in one or another part of the patient's body given the likely and/or «right» dynamics of local values of similar characteristics in the «right» place and in a «right» interval of time. So many modern medical devices and instruments do not have a secure form, dimensions, elasticity, viscosity, friction, temperature, light, other beam's properties and other physical and chemical characteristics. Therefore, at the absolutely flawless application of technological processes of their application does not exclude the appearance of such local tissue damage, as local irritation, an ischemia, a syndrome of prolonged crushing tissue necrosis and perforation, bleeding.

Keywords: *local temperature, illumination, acidity, alkalinity, osmotic pressure, saturation of gases, competitive materials.*

Bioceramic coatings and composites for biomedical applications

R. Gadow, A. Killinger
rainer.gadow@ifkb.uni-stuttgart.de

University of Stuttgart

Bioceramics are bulk, coating and composite materials for use in medical devices and applications, especially for human health care. An important field of application are temporary or permanent implants with mechanical functionality and with tailored or designed surfaces and optimized interfaces to enable the required compatibility. Thermal spray processing like APS, VPS and HVOF are efficient, fast and flexible manufacturing technologies to produce bioceramic coatings, surfaces and layer composite structures.

In recent years new material concepts have been developed for ceramic cell carriers in vitro and even in vivo for the selective formation and growth of special cell cultures with various applications in tissue engineering up to complete substitutes for human organs. Not only the intrinsic material properties in bulk or volume play an important role in these applications but the surface structure, composition and morphology are even more important because of the chemical reactions at the interface.

Bioresorbable polymer implants are a promising concept in maxillofacial surgery, e.g. bone fracture repairing or bone defects replacement, since their use eliminates the need for a secondary operation to remove metal implants. Mechanical properties and biocompatibility of these implants require new composite devices. Thermally sprayed tricalcium phosphate (TCP) coatings can significantly increase the biocompatibility of polymer implants and contribute to match the resorption rate of the device with the bone healing rate, leading to a correct mechanical stress transfer implant/tissue and therefore to successful fracture fixation even in load conditions. TCP is an osteoconductive and bioresorbable ceramic material.

The novel supersonic fast suspension flame spray technique (HVSFS) enables direct processing of submicron and nano sized particles as liquid feedstock suspensions. This workplace and health risk safe processing of nanopowders in suspension opens an entirely new field of spray materials for the production of nano coatings (e.g. mixed phase powders, cermet materials and bioglasses). Due to the very high particle velocity and kinetic impact the deposition of very dense coatings is possible. The traditional gap between conventional thermal spray coatings and thin solid films deposition can be closed, regarding coating thickness (10 – 50 μm) in industrial manufacturing

Keywords: *Bioresorption; Calcium phosphate coatings; Plasma spraying; HVSFS processing, ceramic-polymer composites*

The Fractal Nature in Ceramic Materials Structures

V.V. Mitic^{1,2}, Lj. Kocic¹, V. Paunovic¹

¹University of Nis, Faculty of Electronic Engineering, Nis, Serbia

²Institute of Technical Sciences of SASA, Belgrade, Serbia

It is very well known that we are today in the ages of ceramics civilisation and especially within advanced ceramics materials the BaTiO₃ ceramics with specific electric and electronic properties has a variety of very modern applications. Through our up-to-day research we recognize that BaTiO₃ and similar ceramics have a fractal configuration nature on the basis of three different phenomena. First, ceramic grains have a fractal shape seen as a contour in cross section or as grain's surface. Second, there are so-called "negative space" made of pores and intergranular space. Being extremely complex, the pore space plays an important role in microelectronic, PTC, piezoelectric and other phenomena. Third, there is a process of Brownian--fractal motions inside the material during sintering in the form of flowing micro-particles –ions, atoms, electrons which is an essentially fractal phenomenon. These triple factors, in combination, make the microelectronic environment of very peculiar electro-static and dynamics microelectronic environment. The stress in this note is set on intergranular micro-capacity and micro-impedances and fractal components affecting on overall impedances distribution. Constructive theory of fractal sets explains possible approach in recognizing microcapacitors with fractal electrodes. The method is based on iterative process of interpolation which is compatible with the model of grains itself. Intergranular permeability is taken as a function of working temperature. The main geometric input is outline of BaTiO₃-ceramics grains which is taken from SEM analysis and microphotographs. All of these new fractal frontiers opens a new era in future microelectronic processing and miniaturizations.

Keywords: *BaTiO₃-ceramics, fractals, microstructure, microimpedances*

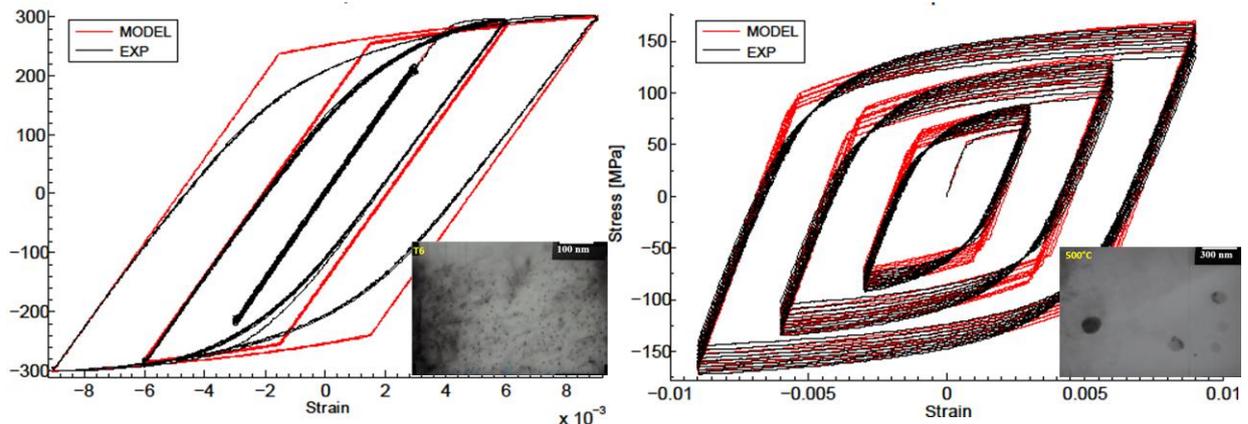
Cyclic behaviour of a 6061-T6 aluminium alloy after transient heat treatments

M. Perez¹, D. Bardel^{1,2}, D. Nelias², S. Dancette¹, P. Chaudet², V. Massardier¹
michel.perez@insa-lyon.fr

¹Université de Lyon, INSA-Lyon, MATEIS UMR CNRS 5510, F69621 Villeurbanne, France

²Université de Lyon, INSA-Lyon, LaMCoS UMR CNRS 5259, F69621 Villeurbanne, France

6061-T6 alloy is submitted to different heat treatment affecting thus the precipitation state. SANS and TEM are used to characterize the precipitation state. In parallel, multi-level cyclic loadings are performed to get the final mechanical properties. The experimental results show a transition of the plastic behaviour from the T6 state (fully precipitated) to the solutionized samples. These hardening evolutions are then modelled thanks to an adaptation of the classical Kocks-Mecking-Estrin formalism coupled with a recently developed size-distribution precipitation model. The proposed modeling approach takes into account (i) the kinematic contribution of grains and precipitates, and, (ii) the classical isotropic contributions on strengthening of dislocations, solid solution and precipitates. Except for the elasto-plastic transition, the model caught very well the kinematic/isotropic transition and the yield stress slope.



Cyclic behavior for two different precipitation state T6 and SS

Keywords: isotropic and kinematic hardening, precipitation, age hardening, cyclic loading, KME

Multiple-Sample Strength Testing within a Centrifuge: Tensile and Compressive Stress Conditions

U. Beck¹, S. Hielscher¹, J.- M. Stockmann¹, D. Lerche², U. Rietz²
uwe.beck@bam.de

¹ BAM Federal Institute for Materials Research and Testing, Division 6.7 Surface Modification and Surface Measurement Techniques; Unter den Eichen 87, 12205 Berlin, Germany

² L.U.M. GmbH, Justus-von-Liebig Str. 3, 12489 Berlin, Germany

Up until a short while ago, tensile and compressive stress tests have been almost exclusively carried out as single-sample tests within a tensile or hardness testing machine. The introduction of centrifuge technology changed this situation in several ways.

Firstly, multiple-sample strength testing is possible now for both tensile load conditions, e.g. determination of composite, bonding respectively adhesive strength, and compressive load conditions, e.g. hardness, compressibility respectively compactibility. Secondly, there is no need for a two-sided sample clamping and double-cardanic suspensions as samples are simply inserted using a one-sided sample support. Thirdly, shear forces can be avoided by means of guiding sleeves which steer test stamps acting as mass bodies for either tensile or compressive load testing. Fourthly, as up to eight samples can be tested under identical conditions within a very short period of time – typically within 15 minutes including sample loading and unloading – a reliable statistical evaluation of strength is feasible now.

The bench-top test system is described in detail and demonstrated that the centrifugal force acts as testing force in an appropriate way and Euler- and Coriolis-force do not affect the testing results in a negative manner. Examples for both tensile strength testing, i.e. bonding strength of adhesives-bonded joints and adhesive strength of coatings, and compressive strength testing, i.e. Vickers-, Brinell- and ball hardness, are presented, discussed and compared with conventional tests within tensile or hardness testing machines. It is shown that centrifuge technology provides more reliable results in a much shorter period of time.

At present, a maximum testing force of 6.5 kN can be realized which results - at diameters of 5, 7 and 10 mm of the test stamp or the adherent – in tensile or compressive stress values of 80, 160 and 320 MPa. This is already beyond bonding strength of cold- and warm-curing adhesives (30 MPa, 100 MPa). Moreover, centrifuge technology is compliant to standards such as EN 15870, EN ISO 4624, EN ISO 6506/6507 and VDI/VDE 2616. Programmable test cycles allow both short-term stress and long-term fatigue tests. It is shown that there is still much more potential of centrifuge technology for a huge variety of applications in both R&D and QC.

Keywords: *multiple-sample strength testing, tensile stress, compressive stress, bonding strength, adhesive strength, hardness, centrifuge technology*

New Multifunctional Glasses and Glassceramics: Design, Properties, and Applications

Nikolay Nikonorov, Vladimir Aseev, Alexander Ignatiev, Elena Kolobkova,
Alexander Sidorov, Pavel Shirshnev
nikonorov@oi.ifmo.ru

Department of Optoinformation Technologies and Materials, ITMO University,
199034, St. Petersburg, Russia

Some novel multifunctional glasses and glassceramics doped with rare earth ions, silver and copper molecular clusters, silver nanoparticles, quantum dots and semiconductor nanocrystals have been developed for photonic and plasmonic applications. Structure and properties of the materials and their applications for photonics and plasmonics have been demonstrated.

The first material presents a luminescent oxyfluoride glass and nanoglassceramics doped with rare earth ions, silver clusters and nanoparticles. The possibility of obtaining nanosized crystals of a new class of PbLnOF_3 compounds, in which Ln are lanthanides from Ce to Lu, with a fluorite structure in a glasslike matrix has been demonstrated. It was shown that all lanthanides from Ce to Lu are incorporated into crystalline phase. Possibility of the utilization of the materials for fiber lasers at 1.5 and 3 μm has been demonstrated. The material can be used as a highly efficient phosphor for white LEDs and light up- and down-converters for photovoltaic solar cells.

The second material presents a potassium-alumina-borate glass host with precipitated Cu-molecular clusters and nanocrystals of CuCl and CuBr. It was shown that the decrease of size of nanocrystals resulted in the decrease of their melting temperature. The nanoglassceramics exhibits good non-linear properties. The material can be used for control optical signals and optical limiters.

The third material presents photo-thermo-refractive glassceramics doped with erbium and ytterbium ions, silver nanoparticles and NaF-AgBr nanocrystals. It is shown that erbium and ytterbium ions stay in glass host after photo-thermo-induced crystallization. The material combines itself several opportunities: fabrication of lasers or amplifiers, recording of highly efficient volume Bragg gratings (spectral filters, WDMs, combiners etc.), and fabrication of planar waveguides or optical fibers.

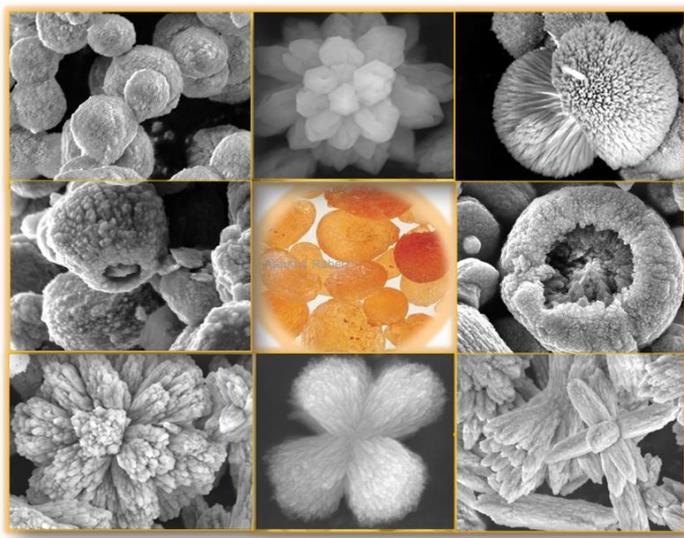
The fourth material presents silicate glass doped with cerium and silver molecular clusters and metallic nanoparticles. It was shown that silver molecular clusters demonstrate an extra broadband luminescence in visible spectral range. The material can be used as a phosphor for white LEDs and a light down-converter for photovoltaic solar cells. It was shown that the glass doped with silver metallic nanoparticles has high absorption coefficient in the spectral range of plasmon resonance. This absorption band depends on shape, size and concentration of the nanoparticles as well as surrounding shell. The material can be used for chemical and biological sensors based on surface plasmon resonance.

Keywords: multifunctional glasses, glassceramics, photo-thermo-refractive

Biomimetic Approach using Natural Gums as Novel Crystal Growth modifiers

Bojja Sreedhar
sreedharb@iict.res.in

Inorganic and Physical Chemistry Division, Council of Scientific and Industrial Research – Indian Institute of Chemical Technology, Hyderabad 500 007, Andhra Pradesh, INDIA



Mimicking nature and designing bioinspired materials represents a promising way to reach technological innovations in many interdisciplinary scientific fields, since biological materials exhibit a high degree of sophistication, hierarchical organisation, hybridisation, efficiency, resistance and adaptability. In recent years, along with the application of biomimetic materials in catalysts, membranes and medical implants, biomimetic synthesis of inorganic materials with specific morphology and size has become an important research area. Researchers with a biological perspective have studied biomineralisation in a variety of systems that utilise many different inorganic base materials. Chemists are increasingly concerned with the synthesis of advanced materials with enhanced or novel properties. Specific molecular interactions at the inorganic/organic interface seem to control nucleation and growth; often stabilizing new modifications and morphologies. Studies have demonstrated that a promising approach is to use organic additives and/or templates to control nucleation, growth, and alignment in the synthesis of inorganic materials. Green strategic routes have been designed to synthesis metal oxide (ZnO) and metal carbonate ($\text{CaCO}_3/\text{BaCO}_3/\text{SrCO}_3$) crystals by simple homogeneous precipitation and low temperature reaction in the presence of different natural gums as crystal growth modifiers and well characterized using XPS, SEM, TEM, XRD, FT-IR, and TG-MS.

Rheo-mechanical Concepts of Development Materials with Extreme Dynamic Strength

¹László A. Gömze and ²Ludmila N. Gömze
femgomze@uni-miskolc.hu

¹University of Miskolc, Miskolc-Egyetemváros, H-3515 Hungary
²Igrex Ltd, Igrici, Rákóczi út 2., H-3459 Hungary

Materials with different crystalline and morphological compositions have different chemical, physical and rheological properties including melting temperature, module of elasticity and viscosity. Examining the material structures and behaviors of different ceramic bodies and **CMCs** under high speed collisions in several years the authors have understood the advantages of hetero-modulus and hetero-viscous complex material systems to absorb and dissipate the kinetic energy of objects during high speed collisions.

Applying the rheo-mechanical principles the authors successfully developed a new family of hetero-modulus and hetero-viscous alumina matrix composite materials with extreme mechanical properties including dynamic strength. These new corundum-matrix composite materials reinforced with **Si₂ON₂**, **Si₃N₄**, **SiAlON** and **AlN** submicron and nanoparticles have excellent dynamic strength during collisions with high density metallic bodies with speeds about 1000 m/sec or more. At the same time in the alumina matrix composites can be observed a phase transformation of submicron and nanoparticles of alpha and beta silicone-nitride crystals into cubic **c-Si₃N₄ diamond-like** particles can be observed, when the high speed collision processes are taken place in vacuum or oxygen-free atmosphere.

Using the rheological principles and the energy engorgement by fractures, heating and melting of components the authors successfully developed several new hetero-modulus, hetero-viscous and hetero-plastic complex materials. These materials generally are based on ceramic matrixes and components having different melting temperatures and modules of elasticity from low values like carbon and light metals (**Mg, Al, Ti, Si**) up to very high values like boride, nitride and carbide ceramics.

Analytical methods applied in this research were scanning electron microscopy, X-ray diffractions and energy dispersive spectrometry. Digital image analysis was applied to microscopy results to enhance the results of transformations.

Keywords: *Ceramics composites, diamond-like, nanostructure, rheology, strength*

Microstructures and properties of thermoelectric silicides

Stéphane Gorsse, Solange Vivès, and Philippe Bellanger
gorsse@icmcb-bordeaux.cnrs.fr

Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS), Pessac 33608, France

Ideally, thermoelectric materials should be thermal insulators and electrical conductors with large Seebeck coefficients. This is a quite antagonist combination of properties.

In this presentation, we will show that metallurgical concepts and phase diagrams can provide design guidance to change the properties. The distinguishing feature of metallurgy is to act at the level of the microstructure. Many materials properties are controlled by the nature of the interactions between the microstructure and the underlying mechanism, for example phonons in the case of thermal conductivity. Therefore, generating and tailoring the nano/microstructure, such as the grain size and morphology, the texture, and the precipitate distribution is one of the main degree of freedom used by the metallurgist to tune the properties, study the behavior of materials, and improve their performance. We will describe two examples: the first concerns a modelling and combinatorial approach applied to quantify the individual effect arising from the nano/microstructure on the lattice thermal conductivity of nanostructured $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ alloys, and the second is related to the crystallographic texture control of higher manganese silicide.

Keywords: *microstructure, metallurgy, thermodynamic, thermoelectrics.*

Quench induced stresses in thick AA7449 aluminium alloy plates: modelling of precipitation and quantitative characterisation using in situ SAXS measurements

N. Chobaut¹, P. Schloth^{1,2}, D. Carron³, H. Van Swygenhoven², J.-M. Drezet¹

¹Ecole Polytechnique Fédérale de Lausanne, Computational Materials Laboratory, 1015 Lausanne, Switzerland

²Paul Scherrer Institut, Swiss Light Source, 5232 Villigen PSI, Switzerland,

³LimatB, Université de Bretagne Sud, Centre de Recherche Ch. Huygens, F-56321 Lorient, France

During quenching, thick industrial heat treatable aluminium alloy plates undergo different cooling paths between the surface and center. Beside large residual stresses thermal gradients cause metallurgical changes of the nanostructure which further affect the internal stress build-up. These ones have been measured in AA7449 plates with different thicknesses using neutron diffraction technique. They are particularly detrimental as plates are machined out to build extrusion moulds for the plastic industry or airplane parts for aeronautics.

The as-quenched microstructure through the plate thickness was studied using small angle neutron (SANS) and X-ray scattering (SAXS) and TEM. Additionally, in situ SAXS experiments were conducted during quenching from the solutionizing temperature to study the formation of second phases during quench. The results are compared with the outcomes of a physical precipitation model calibrated using dedicated SAXS experiments.

Large heterogeneous \square precipitates form at high temperatures and soften the material. At lower temperatures homogeneous precipitates evolve with sizes in the nano-meter range. These clusters/GP Zones strengthen the material during quench and thus increase the residual stresses in the plate. The precipitation model is able to describe the formation of the two precipitate families during quench provided the influence of vacancies on the precipitation kinetics is taken into account. A better quantification of the as-quenched residual stresses is obtained by using a thermo-metallurgical-mechanical model that couples heat transfer during quenching with a yield strength model. This yield strength model uses as input the volume fractions and average precipitate sizes calculated by the precipitation model.

Keywords: heat treatable 7xxx aluminium alloys, precipitation, residual stresses, SAXS, SANS, neutron diffraction.

Solvothermal Synthesis of Morphology Controlled Metal Oxide Particles for Multifunctional Cosmetic Application

Tsugio Sato¹, Shu Yin¹, Takehiro Goto², Takumi Tanaka²
tsusato@tagen.tohoku.ac.jp

¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

² Daito Kase Kogyo Co. LTD., Osaka 535-0005, Japan,

Metal oxides have been used as various functional materials, such as pigments, UV-shielding materials, etc. It is important to control the morphology of the particles to improve the functionality. The morphology controlled particles of CeO₂, ZnO, K_{0.80}(Li_{0.27}Ti_{1.73})O₄ and Al₂O₃ were fabricated in order to improve the multifunctionalities, such as UV-shielding, comfort when applied on the skin, soft-focusing which shows the ability of skin stain concealment, etc. for cosmetic application by solvothermal reactions.

Nanoparticles of Ca²⁺ doped CeO₂ were prepared by the coprecipitation reaction of Ce³⁺ and Ca²⁺ at room temperature followed by the oxidation by H₂O₂. Spherical CeO₂ submicron powders were precipitated by the homogeneous precipitation reaction using Ce(NO₃)₃ and urea mixed aqueous solution at 90°C followed by calcination in air. Plate-like microparticles of CeO₂ were prepared by the reaction of Ce(NO₃)₃ and NaHCO₃ at room temperature followed by calcination in air. Plate-like microparticles of K_{0.80}(Li_{0.27}Ti_{1.73})O₄ were fabricated by flux method using a KCl flux. Morphology controlled ZnO, such as plate-like, rod-like, star-like and spherical ones were formed by solvothermal reactions using Zn(NO₃)₂ as a zinc source and various alkalis and surface modifiers, such as hexamethylenetetramine, monoethanolamine, triethanolamine, ethylene glycol, Fe³⁺, etc. around 80°C. Such morphology controlled ZnO nanoparticles could be homogeneously coated on plate-like mica microparticles by two steps solvothermal reactions. Plate-like microparticles of Al₂O₃ were prepared by the reaction of Al(NO₃)₃ and NaHCO₃ aqueous solutions around 240°C.

The nanoparticles of Ca²⁺ doped CeO₂ showed excellent UV-shielding ability with low oxidation catalytic activity, while the spherical submicron powders and plate-like microparticles of CeO₂ showed the excellent comfort when applied on the skin. The plate-like microparticles of K_{0.80}(Li_{0.27}Ti_{1.73})O₄ showed excellent comfort and glory characteristics. Coating CeO₂ nanoparticles on plate-like microparticles of K_{0.80}(Li_{0.27}Ti_{1.73})O₄ was useful to improve the comfort without loss of the UV-shielding ability. The rod-like and star-like ZnO particles showed excellent soft focus property as well as excellent UV-shielding ability. The morphology controlled ZnO nanoparticles coated mica showed excellent soft focus property and UV-shielding ability without loss of excellent comfort. Plate-like microparticles of Al₂O₃ also showed nice comfort. These morphology controlled oxide particles may be useful as multifunctional materials for cosmetics.

Keywords: *solvothermal reaction, oxide particles, morphology control, UV-shielding, comfort, soft focus, concealment*

Polymer Derived Ceramics – A Versatile Concept of Material Processing

Michael Scheffler
m.scheffler@ovgu.de

Institute for Material and Joining Technology, Otto-von-Guericke-University Magdeburg,
Magdeburg, Germany

Research and development of polymer precursors and their conversion into polymer derived ceramics (PDCs) started some 40 years ago. During this time a huge variety of manufacturing protocols have been developed involving the steps shaping, cross-linking and pyrolysis; parts with a size spanning over several orders of magnitude are available with a desired microstructure and their resulting functionality. Over the years, the ceramic yield after pyrolysis, the size of parts, the shrinkage behaviour during pyrolysis, shaping and microstructure development as well as the macrostructure remained main issues in PDCR&D. And novel applications have been identified to be realized with PDCs. In the first part, this paper will give an overview of the concept of polymer derived ceramics. The second part deals with results from recent research activities and in the third part the focus will be set on polymer derived ceramics from polysiloxane precursors. Some potential applications will be discussed and an outlook will be given.

SESSION 1

Advanced Materials for Bio- and Medical Applications

Thermoplastic properties productions of synthetic polymers for medical applications

Anton Kasatkin
ant-kasatkin@yandex.ru

Department of Pharmacology, Izhevsk State Medical Academy, 426034 Izhevsk, Russia

The study of effect temperature and acidity of medicinal agents to change the elastic properties of intravascular catheters size 18G, made of polyurethane, Teflon and silicone. Elastic properties of catheters were determined by measuring the length of the deflection (in mm) arising after exposure to the free end of the tube by force of 20 newtons. Measuring the deflection of the catheter tube was performed under the conditions of incubation for 10 minutes at +25.0, +30.0, +36.0 and +42.0 °C, before and after 24 hours incubation with the drug solution in the range acid from 3.0 to 9.0. During the studies found that the temperature change affects, and the change in pH does not affect the elasticity of the catheters. Moreover, cooling increases the elasticity of the catheters, but in different ways, depending on the polymeric materials from which catheters are made. Thus catheters formed of Teflon, were more elastic than catheters of polyurethane and silicone in all temperature conditions. In particular, at +42 °C the deflection of teflon catheter was equal $13,7 \pm 0,3$ mm ($P \leq 0,05$, $n = 10$), while the catheters made of polyurethane and silicone - $24,9 \pm 0,4$ mm ($p \leq 0,05$, $n = 10$) and $38,4 \pm 0,3$ (respectively).

Additionally, in experiments on conscious pigs and clinical observations of patients, it was shown that all modern catheters made of silicone, polyurethane and Teflon, cause damage to the endothelium of veins within a few minutes after their catheterization. Consequently, modern catheters have extremely high elasticity both at room temperature and at human body temperature, which is the cause of their high physical aggressiveness.

To enhance the security of vascular catheters is no alternative of their manufacturing of plastic material, which deprives them of elasticity at human body temperature. To this end, we previously developed a new intravascular catheter [1]. Using a new catheter with acquired at +33 °C stretch, soften and floating properties, and the application of new technology vein catheterization has reduced the likelihood of damage to the venous endothelium and development of postinjection complications [2,3].

Keywords: *new intravascular catheter, elasticity, physico-chemical properties, postinjective complication, thechnology of catheterization.*

References

- [1] Urakov, A.L. et al. Method for ulnar vein catheterisation and multiple-dose intravenous drug introduction. Patent RU 2387465.
- [2] Urakov, A.L., Urakova, N.L., Kasatkin, A.A. 2013. Improving the safety of intravenous injections. *Voenno meditsinskii zhurnal*. №9. 73-75
- [3] Urakov, A.L., Urakova, N.L., Kasatkin, A.A. 2012. Method of effective and safe use intravenous catheter. *Modern problems of science and education* №4. URL: <http://www.science-education.ru/en/104-6687>, (date of access: 11.12.2013).

Artificial food lump from porous neoprene and the method of its use for the evaluation of adaptation patients to the dental constructions

Mikhail Soiher¹, Aleksey Reshetnikov², Maxim Kopylov¹
msoiher@yandex.ru

¹Institute of Biotechnology and Interdisciplinary Dentistry, 123995, Moscow, Russia
²Izhevsk State Medical Academy, 426034 Izhevsk, Russia

Immediately after the insertion of the new dental construction to a patient evaluation of its fitness to mastication and the patient adaptation to the construction is provided. For this purpose special instant diagnosis, based on registration of radiant heat from oral cavity tissues, which is carried out with help of infrared thermography of oral cavity tissues after the mastication of oral "mastication reference", has been developed. The artificial food lump, providing reference mastication loading in the oral cavity is provided as the mastication reference. The mentioned above artificial food lump as elastic, nondestructive, it has food substance taste and stabile springiness.

The artificial food lump has spherical shape, it is identical to the formed by mastication of fresh bread by an adult person food lump by size and shape. The lump is the 1 cm cylinder with two 4 cm semi-spheres at edges, on one of them there is a plaiting thread with a clip at the end. The clip provides the taking out the lump by accidental getting it to esophagus or fissure of glottis. The lump has reference elastic features, which are stable by mastication, and it is harmless for the patient and dental constructions. Elastic base of the artificial food lump is porous neoprene with porosity not more than 30 %. The filling for porous neoprene is air

The instant diagnosis of patient adaptation to dental constructions is that there are two artificial food lumps, heated to +37°C. The first lump is applied before, and the second lump is applied after the insertion of dental constructions. In both cases the patient is asked to put the lump into his mouth and masticate it for 30 sec, moving it through the dental arch. After the mastication of each lump, lumps are removed and undergo the investigation of radiant heat of the oral cavity tissues dynamics with help of thermovisor. Thereby the absence of hyperthermia or short-time uniform symmetrical temperature increase in oral cavity tissues after the first lump mastication show high adaptation of the patient to mastication and high resistance of the patient to the dental construction, the decision concerning possibility of the secure insertion is made, The insertion of the dental construction is made under control of dynamics of radiant heat of oral cavity tissues after 30 sec mastication of the second identical artificial food lump. After this radiant heat dynamics is compared with the first one, elevation of temperature shows low adaptation of the patient to the dental construction and possibility of tissue damage.

Keywords: *adoption, artificial food lump, mastication reference, dental construction.*

Intestinal probe that is becoming soft on the inside of the intestine newborns

Aleksandr Urakov^{1,2}, Natalia Urakova²
urakoval@live.ru

¹Department of the thermal deformation processes, Institute of Mechanics of the Ural Branch of the RAS, 426067, Izhevsk, Russia

²Department of General and Clinical Pharmacology, Izhevsk State Medical Academy, 426034 Izhevsk, Russia

Melting intestinal probe is completely filled with special food gelatin, which at room temperature keeps a high elasticity, and at temperatures above 30°C. Therefore, at room temperature intestinal probe has sufficient hardness and high elasticity. Moreover, the hardness of the probe increases at lower temperatures, which allows to manage of the hardness and of the degree of elasticity of a probe by pre-cooling to the 'right' temperature. In this regard, before applying the probe to be cooled to the desired temperature, it will ensure that the "right" firmness. Cooling intestinal probe and make it up to the desired hardness then provides its introduction into the small intestine through the nose, down the esophagus and stomach to the selected portion of the small intestine. Accommodation solid intestinal probe inside the child's body at a temperature above +30°C leads to heating and melting of solid material, which filled the cavity gastrointestinal probe. After 15 minutes the solid material in the cavity of the gastrointestinal probe turns into easy-flowing liquid. This liquid is easily follows from the probe and therefore, in 15 - 20 minutes probe completely loses its elasticity and acquire high elasticity and softness, which provides introduction of nutrients in the intestines, saves seams intestinal anastomosis and provides decompression in the gut cavity after surgery on it.

The matter is that modern intestinal probes are a polihlorvinilovuju tube having excessively thick wall, which at long storage hardens and ensures the preservation of shape and volume of the probe practically forever including at body temperature. Therefore, the introduction of such a probe in the nose and throat, esophagus, stomach and intestines are inevitable tip sections, which stubbornly opposed physiological bends and therefore lead to a syndrome of prolonged excessive pressure fabrics (for bedsores) the walls of the upper respiratory tract and/or gastrointestinal tract due to the pronounced pressure on the tissues in these areas. The most aggressive action on the rectum provides end-the end of the working part of the intestinal probe, which most other areas of the probe causes sore in the intestinal wall, her perforation and peritonitis.

It contrast that, our intestinal probe at body temperature can turn into a soft tube, which ceases to aggressive action on the wall of the intestine with the long term in it. In particular, such a soft intestinal probe virtually no pressure on the wall of the intestine in its hinges and does not compress it blood vessels. Therefore, even for long stays in the gut (for 3 - 7 days) melting intestinal probe does not cause ischemia syndrome of prolonged excessive pressure necrosis of tissues and parcel of the bowel wall. Because of this melting intestinal probe does not cause ulcer perforation and peritonitis.

Keywords: *intestinal probe, variable temperature elasticity, surgery, newborn children.*

Role of Microorganisms and Magnetite Nanoparticles in Metal Adsorption released from E-waste

Gayatri.Y¹, Shailaja Raj.M¹
shailarm@yahoo.com

Department of Microbiology , St.Francis College for Women, Hyderabad, India

Electronic Waste or E-waste is the term used to describe products such as computers, laptops, TVs, DVD players, mobile phones, mp3 players etc. which have been disposed into the environment. Electrical and electronic equipment are made up of a multitude of components, some containing toxic substances. If these are left untreated and disposed in landfills or not recycled by using proper methods of recycling, they leach into the surrounding atmosphere, soil and water and cause adverse effects on human health and environment. Many elements of this waste contain poisonous substances such as lead, tin, mercury, cadmium and barium, which cause severe diseases like cancer, birth defects, neurological and respiratory disorders. Informal processing of electronic waste in developing countries causes serious health and pollution problems.

The present study focuses on metal adsorption studies by microorganisms isolated from E-waste soil dumping yards and magnetite nanoparticles. Microorganisms were collected from four different areas such as Maheshwaram, Shameerpet, Musheerabad and Jawaharnagar dumping yards in and around Hyderabad, India. Gram positive bacilli and cocci were isolated and identified by biochemical methods. Since Iron-based magnetic nanomaterials (Magnetite) have unique properties, such as larger surface area-volume ratio, diminished consumption of chemicals, and no secondary pollutant were synthesized by co-precipitation process and further used for adsorption studies. Magnetite nanoparticles were characterized by XRD and the size was determined to be 99nm. Lead an important component of many electronic goods was undertaken for adsorption studies by bacteria isolated from E-waste soil and magnetite nanoparticles using Atomic adsorption spectrophotometer. Effect of different metal concentrations ranging from 5ppm to 20ppm was analyzed. It was observed that metal adsorption by magnetite nanoparticles was more at 15ppm concentration which is 162.83mg/L and by bacteria greater adsorption was observed at 5ppm which is 151.89mg/L where the initial metal concentration is 173.95mg/L . Contact time studies also emphasized greater adsorption at 30min, 4h and 24h by both magnetite nanoparticles and bacteria. Metal adsorption was higher by magnetite nanoparticles when compared to bacteria isolated from E-waste soil.

Hence the present study is proposed to explore bacteria for the determination of their tolerance capacity in and around the areas of Hyderabad where heavy metal ions are leached and also to prepare microbial iron nanocomposites which can act as potential geoactive agents.

Keywords: *E-Waste , Magnetite nanoparticles , Heavy metals , Adsorption studi*

Phase content and properties of ZrO₂(Mg) - MgO system sintered at wide temperature range

Ales Buyakov, Sergey Kulkov
alesbuyakov@gmail.com

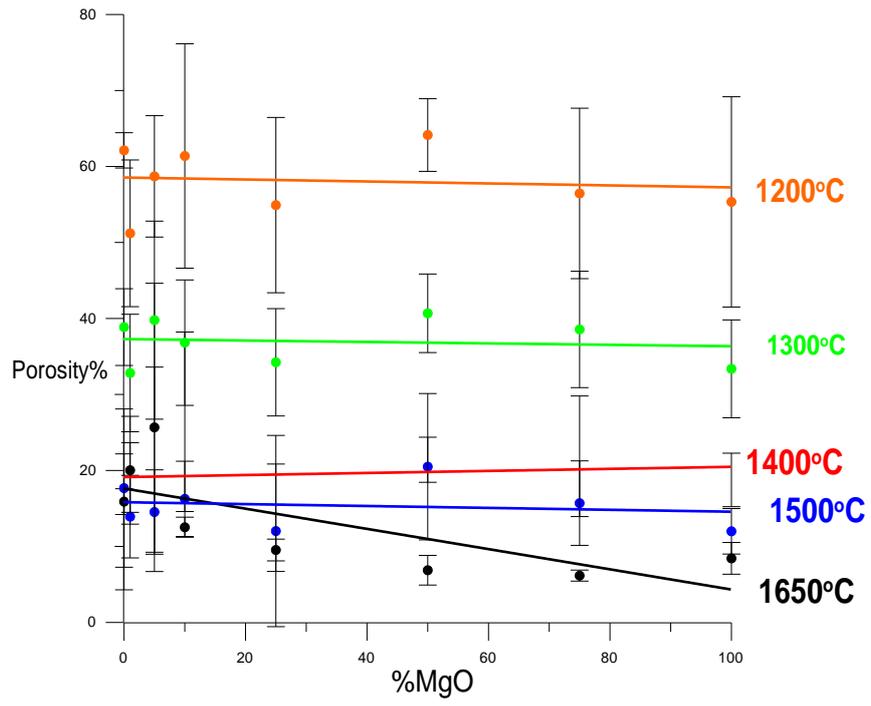
ISPMS SB RAS, Laboratory of Physics of Nanostructural Ceramic Materials

Nowadays medicine is one of the most actively developing directions of using ceramic materials. It used for making instruments, filtration of biological drugs, stomatology and endoprosthetics, that deserve special attention. Unlike the organic compounds and metals, ceramics has identical type of chemical bond with inorganic bone matrix, which significantly reduces the risk of rejection.

Zirconia included in the register of ISO as the material allowed to be used for the manufacture of osteoimplants. Zirconia products have high strength and toughness under ambient and elevated temperatures, and therefore suitable for the loaded and wear-resistant applications. However, in a pure zirconia monoclinic phase transforms into tetragonal under heating, that accompanied of volume increase, cracking and strength deterioration. Stabilization of zirconia consists in rebuild of tetragonal phase to cubic and occurs with adding a alloying material such as MgO, which has a great fracture toughness. Completely stabilized zirconia is a cubic solid solution. Crystal lattice has strong stable connections, which can not be destroyed by heat treatment up to 2500°C. Besides that magnesium is a biologically active material. MgO participates in protein synthesis, accelerates bone tissue regeneration, and gives osteoconductive properties to implant surface.

Studies were carried out over the mixtures of stabilized zirconia and magnesia powders in various proportions from pure ZrO₂ to pure MgO. Cylindrical specimens were made 10 mm in diameter and a height of 10-13mm. Magnesium oxide was in two conditions into them: as a substitutional solid solution in stabilized zirconia and as unbound molecules of MgO. The first part of the samples was subjected a heat treatment at 1650°C, the second - in 1500°C, then the temperature was decreased in steps of 100°C to 1200°C.

Porosity is one of the most important properties for osteoimplants. After heat treatment it became clear that composite porosity decreases with the amount of added MgO for samples sintered at 1650°C. At 10% MgO porosity of composite is about 13% and at 75% MgO porosity nearly to 10%. For the rest temperatures level of porosity is almost constant with increasing amounts of MgO, but significantly increases with a decrease of temperature and at 1200°C is about 58%.



Researches of mechanical behavior of bone tissues for development and selection of individual ceramic implants

Tatyana Kolmakova^{1,2}, Sergey Kulkov^{1,2}, Svetlana Buyakova^{1,2}
kolmakova@ftf.tsu.ru

¹Institute of Strength Physics and Materials Science (ISPMS) SB RAS, 634021 Tomsk, Russia

²Tomsk State University, 634050 Tomsk, Russia

Along with the requirement of biocompatibility applied to bone implants, there is also a need to ensure their mechanical similarity of bone tissue to avoid possible bone resorption on the boundary of bone-implant when their installed in vivo. Mechanics problems, arising from the creation of biological tissues implants are solved on the basis of studies of the structure and mechanical properties of the biological tissues and include the establishment of basic requirements for substitutes in terms of mechanics of implants materials. Computer researches of mechanical behavior of fragments of the bone containing compact and spongy bone tissue of different density and the mineral contents were conducted, at axial compression. Mechanical parameters to which have to satisfy osteoimplants were obtained.

Keywords: *osteoimplants, compact bone tissue, spongy bone tissue, mechanical similarity*

The XAS and DFT studying of Pt based anticancer drugs in the biological systems.

Victoria Mazalova¹, Oleg Polozhentsev¹, Aram Bugaev¹, Alexander Soldatov and Alexey Maximov²
mazalova@sfnu.ru

1Department of Physics, Southern Federal University, 344090 Rostov-on-Don, Russia
2 Rostov Institute of Oncology, 344000 Rostov-on-Don, Russia

Nowadays, chemotherapy is one of the main treatment methods of cancer. Commercially available cisplatin, carboplatin and oxaliplatin have some serious disadvantages (e.g. not all tumors can be cured, high damage of healthy cells, etc.). There are intensive research efforts to develop new, low-cost and efficient anticancer compounds based on Pt coordination complexes. These compounds kill tumor cells by inhibition of DNA synthesis. Most probable model of this inhibition process is bridging with guanine base. But in order to create a new route for synthesis of novel drugs and decrease their damage influence on the healthy cells one need to get deeper insight into interplay between a local atomic and electronic structure and functional activity of the Pt compounds.

Experimental study of Pt-based drugs (cisplatin, carboplatin, oxaliplatin) interaction with the proteins (human serum albumin, HSA) and nucleic acids of DNA on the basis of X-ray absorption spectroscopy (XAS) in near-edge region was performed at KMC-2 beamline of the BESSY-II synchrotron in Berlin. XAS technique proved sensitive to study the local atomic structure around Pt atom of the above mentioned drugs and could be used for studying the interaction of the Pt-based drugs with solutions (applicable for cancer treatment), proteins and nucleic acids. The local atomic structure around the Pt atoms was studied by a theoretical X-ray absorption near-edge structure (XANES) analysis. In order to understand the mechanism of the interaction between the Pt compounds and biological systems, Density Functional Theory (DFT) simulations were performed.

Keywords: XANES, atomic and electronic structure, multiscale computer modelling, anticancer drugs

Study of deformation and fracture of ceramic composites based on nanocrystalline metal oxides. Computer simulation in the framework of movable cellular automaton method

Igor Konovalenko, Chingis Toktohoev, Vladimir Promakhov, Ivan Konovalenko, Sergey Psakhie
igkon@ispms.tsc.ru

Institute of Strength Physics and Materials Science of the Siberian Branch of the Russian Academy of Sciences, 634021 Tomsk, Russia

In the framework of movable cellular automaton method (MCA) a multiscale model of ceramic composites based on nanocrystalline metal oxides with phase transformations in their structure during mechanical loading was developed. On the basis of developed model the mechanical behavior of ceramic composites based on nanocrystalline oxides of zirconium and aluminum with different contents components under uniaxial compression was investigated. For numerical investigations 2D square specimens with the size 32 mkm were generated. The volume content of each component was varied from 20% to 80%. At the interface between components assumption of perfect contact conditions was made. Mechanical properties of the model material corresponded to that of nanocrystalline ceramics $ZrO_2(Y_2O_3)$ and Al_2O_3 with a porosity of 2%. The speed of loading was 0.5 m/s. The problem was solved under plain strain conditions. Accounting for phase transitions in the model was carried out under the proposed phenomenological approach, implying the formulation of the law of inter-automaton interaction corresponding to the irreversible behavior of the material. This law has been chosen so as to correspond to qualitative and quantitative deformation diagrams of $ZrO_2(Y_2O_3)$ with structural transformations. An increase of fracture toughness of zirconia ceramics under implementation of phase transitions were taken into account by introducing a pair of automaton transition kinetics from the "linked" state to the "unlinked" one. To do this, the crack propagation rate parameter was explicitly introduced at the MCA method. It was capable to slow down the transition of automaton pair to "unlinked" state for several time steps. Usually in the MCA method this transition occurs at the one time step, which corresponds to crack propagation with the speed of longitudinal sound. In this model (for the pairs automata modeling phase transition), the value of crack propagation velocity was lower than the velocity of sound in the material. Within the framework of the model constructed main mechanisms of deformation and fracture of composites were studied. The interrelation of structure, mechanisms of fracture and effective strength and elastic properties of the composite was shown.

This study was partially supported by the Russian Foundation for Basic Research, Project № 12-08-00379-a and by the Grant of the President of the Russian Federation for the state supporting young Russian scientists, Project MK- 5883.2014.8.

Keywords: *ceramic composites on the basis of metal oxides, phase transformation, deformation and fracture, computer simulation, movable cellular automaton method*

Comparative Study on Histological Analysis of Biodegradable Magnesium and Magnesium Alloys

Kang-Sik Lee¹, Hyung-Seop Han², Jee Hye Lo Han², Yu-Chan Kim², Hyun-Kwang Seok², Jee Wook Lee³ and Dong-Ho Lee¹
knifebrd@hanmail.net

¹Orthopedic Surgery, University of Ulsan College of Medicine, Asan Medical Center,
Seoul 138-736, Republic of Korea

²Central for Biomaterials, Korea Institute of Science and Technology,
Seoul 136-791, Republic of Korea

Recently, there have been significant advances in development of biodegradable magnesium alloys as orthopedic implant materials. The results of various reported studies have shown that the implants made of magnesium alloys degrade in physiological settings while promoting positive new bone growth. However, there are currently no standardized methods available in the literature to reflect on to perform the histological evaluation of the magnesium and the unique corrosive characteristic of magnesium often hinders the accurate observation. The purpose of this study was to evaluate the four most commonly used bone histological staining methods to observe their effectiveness when used on magnesium. The samples of magnesium were stained with different solutions and weight loss was measured to determine the corrosive nature of each solution. In vivo histological evaluation of magnesium implanted on a femoral condyle of New Zealand white rabbits was then performed to validate the preliminary weight loss measurement results. The result from this study provides the most effective staining method for the histological evaluation of newly developed magnesium implants.

Keywords: *biodegradable metal, magnesium alloy, histology*

Electrochemical behavior of 45S5 bioactive ceramic coating on Ti6Al4V alloy for dental applications

M. M. Machado López¹, M. I. Espitia Cabrera², J. Faure³, M. E. Contreras García¹
eucontre@gmail.com

¹Instituto de Investigaciones Metalúrgicas, UMSNH, C.U. Edificio "U", Morelia, Michoacán, México.

²Facultad de Ingeniería Química, UMSNH, C.U. Edificio "E", Morelia, Michoacán, México.,

³INSERM UMRS-926 Laboratoire de Microscopie Electronique Analytique 21 rue Clement ADER
51685 REIMS cedex, France.

Titanium and its alloys are widely used as implant materials because of their mechanical properties and non - toxic behavior. Unfortunately, they are not bioinert, which means that they can release ions and can only fix the bone by mechanical anchorage, this can lead to the encapsulation of dense fibrous tissue in the body. The bone fixation is required in clinical conditions treated by orthopedic and dental medicine. The proposal is to coat metallic implants with bioactive materials to establish good interfacial bonds between the metal substrate and bone by increasing bioactivity. Bioactive glasses, ceramics specifically 45S5 Bioglass, have drawn attention as a serious functional biomaterial because osseointegration capacity. The EPD method of bioglass gel precursor was proposed in the present work as a new method to obtain 45S5/Ti6Al4V for dental applications. The coatings, were thermally treated at 700 and 800°C and presented the 45S5 bioglass characteristic phases showing morphology and uniformity with no defects, quantification percentages by EDS of Si, Ca, Na, P and O elements in the coating scratched powders, showed a good proportional relationship demonstrating the obtention of the 45S5 bioglass. The corrosion tests were carried out in Hank's solution. By Tafel extrapolation, Ti6Al4V alloy showed good corrosion resistance by the formation of a passivation layer on the metal surface, however, in the system 45S5/Ti6Al4V there was an increase in the corrosion resistance; i_{corr} , E_{corr} and corrosion rate decreased, the mass loss and the rate of release of ions, were lower.

Keyword: *ceramic biocoating, bioglass, corrosion resistance*

References

- [1] A. Balamurugan, G. Sockalingum, J. Michel, J. Fauré, V. Banchet c, L. Wortham, S. Bouthors, D. Laurent-Maquin, G. Balossier, Synthesis and characterisation of sol gel derived bioactive glass for biomedical applications, *Materials Letters*, vol. 60, 2009, 3752-3754.
- [2] L. Ding, Y. Fuqian, J. Nychka, Indentation-induced residual stresses in 45S5 bioglass and the stress effect on the material dissolution, *Engineering Fracture Mechanics*, vol. 75, 2008, 4898–4900.
- [3] F. Pishbin, A. Simchi, M.P. Ryan, A.R. Boccaccini, Electrophoretic deposition of chitosan/45S5 Bioglass® composite coatings for orthopaedic applications, *Surface & Coatings Technology*, vol. 205, 2011, 5260-5262.
- [4] M. Plewinski, K. Schickle, M. Lindner, A. Kirsten, M. Weber, H. Fischer, The effect of crystallization of bioactive bioglass 45S5 on apatite formation and degradation, *Dental Material*, vol. 29, N° 12, 2013, 1256-1264.

Enhanced Photocatalytic Activity of Nanostructured Mesoporous TiO₂-Al₂O₃ coatings on glass fibers for water purification

F. Magana Arreola¹, M. I. Espitia Cabrera², S.E. Borjas Garcia³, A. Medina Flores¹,
M. E. Contreras García¹
eucontre@gmail.com

¹Instituto de Investigaciones Metalúrgicas, UMSNH, C.U. Edificio "U", Morelia, Michoacán, México.

²Facultad de Ingeniería Química, UMSNH, C.U. Edificio "D", Morelia, Michoacán, México.,

³IFM UMSNH, C.U. Edificio "C-3", Morelia, Michoacán, México

The need of new materials to enable the purification of drinking water and decontamination of waste water with advanced low cost technologies is increasing day by day. The porous ceramics can be used in catalysis, photocatalysis, separation and for the immobilization of biological molecules, and even microorganisms, for filtration and bioreactor applications. Regardless of the scale Titania maintains its photocatalytic activity but it can be low due to the high pair-hole recombination rate and the fact that it can be only excited under UV irradiation because its band gap value of 2.9. These problems can be solved using Titania nanoconjugates, as Titania-Alumina nanocojugate that have probed to low the Titania band gap in order to allow it to be excited with lower wave length radiations[2]. In this work, mesoporous nanostructured TiO₂-Al₂O₃ photocatalyst coatings on glass fibers with high specific surface area and low band-gap were obtained by dip coating deposition method. The mesoporous structure was obtained by molecular self-assembling using Tween 20 as template agent in the sol-gel synthesis. The mesoporous nanostructure was characterized by using SEM, TEM, DRX and BET techniques. The obtained coatings presented high specific surface areas and exceptional superior behavior in methylene blue degradation under UVvis and Visible light irradiation reaching up to 99% of MB degradation under UVvis irradiation and up 66% of MB degradation under visible light irradiation in two hours. This enables the possibility to have effective water purification only under sunlight irradiation.

Keywords: *Titania Alumina Photocatalyst, Low band gap titania-alumina photocatalyst, high MB degradation*

Making bioceramic 'alive' by self-powered capillary supply of nutrients through built-in nanochannels

Ki Tae Nam¹, Hae Lin Jang¹, Jin Ho Kim², Hye Kyoung Lee¹, Hyo-Yong Ahn¹, Sunghak Park¹, Malcolm L. Snead³ and Jimmy Xu²
nkitae@snu.ac.kr

¹Department of Materials Science and Engineering, Seoul National University, Seoul, 151-744, Korea

²School of Engineering and Department of Physics, Brown University, Providence, RI 02912, USA

³Center for Craniofacial Molecular Biology, Herman Ostrow School of Dentistry, University of Southern California, Los Angeles, CA 90033, USA

Tree-like circulatory system in living organisms can efficiently supply fluid and nutrient to every part of the body by using hierarchically organized tubes with gradually modified channel geometry. Bone harnesses such an ordered network from micrometer scale to nanometer scale for supplying nutrients and growth factors to its peripheral tissues. In this research, we designed and developed a bone implant platform based upon the concept of a self-powered, pore-gradient driven capillary transport network and showed that supply power of nanochannels can be sufficiently effective in support of small organisms. The creation of a graded pore network in hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) bioceramic was achieved by applying additional pressure energy during sintering where stronger polymer phase-segregation phenomenon under higher pressure energy yielded larger interconnected pores. Notably, our resulting bioceramic with built-in nanochannels had a mechanical strength similar to natural human bone. Finally, we demonstrated that human osteoblast cells proliferated and differentiated on the bioceramic by depending solely on the self-powered supply of fluids and nutrients through these capillary networks to the implant surface.

Keywords: *nanochannel, bioceramic, bone, implant, hydroxyapatite, nutrient supply*

Experimental Investigation of Plasma-Immersion Ion Implantation Treatment for Biocompatible Polyurethane Implants Production

Roman Iziumov¹, Anton Belyaev¹, Vladislav Solodko², Alexey Kondyurin³, and Irina Osorgina⁴
izumov@icmm.ru

¹Institute of continuous media mechanics UB RAS, 614013 Perm, Russia

²Perm State National Research University, 614990 Perm, Russia

³University of Sydney, School of Physics, Faculty of Science, NSW 2006 Australia

⁴The Institute of Natural Science of Perm State National Research University, 614990 Perm, Russia

This work is devoted to the investigation of properties of polyurethane which is used in the production of implants. Depending on the application, the materials have different requirements. In our case we consider implants which surrogate elastic tissues of the human body such as breast implants or interphalangeal joint prosthesis. One of the most important characteristics of the implant material are biocompatibility, elasticity, durability and nontoxicity. Polyurethane satisfies almost all requirements, but it needs treatment to be biocompatible. In our research we used a technique of plasma-immersion ion implantation (PIII) for this goal. The main object of the study was carbonized layer at the surface of the material, which is obtained by PIII-treatment. This layer makes treated material biocompatible but at the same time makes it more stiff. Thus the goal of our investigation was to find the optimal mode of PIII-treatment that allows to obtain sufficiently biocompatible material keeping its other initial properties.

Experimental investigations include set of PIII-treatments of polyurethane specimens in different modes varying the time and intensity of the ion flux. One part of specimens was studied using X-ray photoelectron spectroscopy that enabled to determine the chemical composition of surface layer. Another part of specimens was used for the investigation of the surface energy kinetics, that allowed us to better understand the physical basis of the formation mechanism of a biocompatible layer. The third part of specimens was studied by microscopy to estimate the continuity of carbonized layer. The last part of specimens was implanted to living animal organism for testing material biocompatibility.

As a result we carried out deep experimental analysis of polyurethane characteristics with various types of carbonized layer. It was proposed optimal parameters of PIII-treatment for the production of a biocompatible material, that can be used to surrogate the elastic body tissues.

Keywords: *biocompatibility, implant, polyurethane, plasma-immersion ion implantation (PIII), X-ray photoelectron spectroscopy (XPS)*

Polyurethane finger interphalangeal joint endoprosthesis after ion-plasma treatment behavior modeling

Anton Beliaev¹, Sergey Lebedev¹, Alexander Sokolov²
belyaev@icmm.ru

¹Laboratory of Micromechanics of Structural and Heterogeneous Media, Institute of Continuous Media Mechanics, Ural Branch of Russian Academy of Sciences, 1 Acad. Korolev Street, 614013, Perm, Russia

²Department of Continuous Media Mechanics and Computer Technology, Perm State National Research University, 15 Bukirev Street, 614990, Perm, Russia

The paper deals with a change in mechanical properties of polyurethane after ion-plasma treatment. We propose a model that explains this effect at the micro level. Finite element scheme for calculating the endoprosthesis stress-strain state under conditions close to the real is developed. These models allow us to relate the behavior of the polyurethane at the micro and macro levels and to design the optimal shape of the prosthesis. Implants intended for long-term usage within the human body need complete chemical and biological compatibility and require close integration in human tissue. Ion-plasma treatment of the surface of the polyurethane allows us to obtain carbonized layer, which in return enables to manufacture bioactive implants. In addition to biocompatibility, mechanical compatibility of implants is also required. Elastic and strength properties of the implant material should be sufficient to ensure that the functional mechanical loads do not cause its destruction, which can lead to bone resorption or necrosis (local death of tissue). This paper considers the problem of using finger joint prosthesis with the working part is made from a polyurethane material and covered with a layer of carbon. Deformation of the implant leads to the fact that the carbonized layer on the entire surface cracks. The further deformation leads to the formation of the cracks and emerging of scales from the carbonized layer. Gaps between scales play the role of stress concentrators for a polyurethane substrate. It can lead to development of residual deformations and destruction of the material. In this regard the computer experiments were carried out using the finite element method to evaluate the impact of the carbonized layer on the stress-strain state of the polyurethane prosthesis. Influence of the carbonized layer after cracking on the stress-strain state of the polyurethane was investigated on models with periodicity cell consisting of a substrate with carbon plates. Plates in the model represent scales of the cracked carbonized layer. Stress and strain of polyurethane substrate in places of stress concentration (between fragments of the layer) was evaluated. The study was conducted on scales comparable to micrometers. Computational experiments allowed us to explore changes in strain at stress concentrators regions. Computational experiments of loaded state of finger joint prosthesis allowed us to quantify the stress and strain fields in the material deformation. Comparison with the results obtained on the periodicity cell allowed to establish a connection between the degree of cracking of the carbon layer and layer fragments damaging effect on the polyurethane material.

Keywords: *polyurethane, finite-element method, ion-plasm treatment.*

This work was supported by the Russian Foundation for basic research (a grant 13-01-96009_r_ural_a and a grant 14-08-96003_r_ural_a) and the Ministry of Education of Perm Region under agreement (S-26/632).

Synthesis of Nanocomposites in treatment of Dental Plaques

Anitha Thomas, M. Shailaja Raj
anitha.thomas@sfc.ac.in

¹ Department of Microbiology, St Francis College for Women, Begumpet, Hyderabad.

Dental implant research has been considered with the biocompatibility of materials for implantation. Statistics show that 69% of adult aged 35 to 44 have lost permanent tooth due to accident, gum disease failed root canal or tooth decay. Dental plaque is a general term for the diverse microbial community (predominantly bacteria) found on tooth surface, embedded in matrix of polymers of bacteria, salivary origin. The resin based dental composites commonly used in restorations result in more plaque accumulation than other materials. Nanoparticles considered being of a size not greater than 100 nm and the exploitation of their unique attributes to combat infection has increased in the past decade. The present study deals with the antimicrobial studies of nanocomposite preparations of Titanium dioxide and Zinc oxide and also Titanium dioxide and Silver. Titanium dioxide, Zinc oxide and silver nanoparticles are found to be effective in inhibiting the growth of bacteria. So the present work is to prepare nanocomposites of these oxides and find out if the effectivity is more when the composites are used in dental implants. Some nanocomposite materials have been shown to be 1000 times tougher than the bulk component materials. Earlier studies demonstrates that zinc oxide nanoparticles (ZnO-NPs) blended at 10% (w/w) fraction into dental composites display antimicrobial activity and reduce growth of bacterial biofilms by roughly 80%. The focus of this research is to prepare composites which have improved potentiality in terms of their antimicrobial activity. Thus these nanocomposites which would surely pose a solution to dental implant surgery.

Keywords: *Nano composites, antimicrobial activity, implant surgery.*

Biocompatible polyurethane films

Irina Osorgina¹, Sergey Plaksin², Ilya Morozov³, Vladimir Shadrin³
osorgina@psu.ru

¹National research University, Perm, Ul. Bukireva, 15, Russian Federation

²Perm state medical Academy, Perm, Ul. Siberian, 13, Russian Federation

³Federal state institution of science " Institute of continuous media mechanics UB of RAS, 614013, Perm, street AK. Queen D.1. Russian Federation

Polyurethane films of 0.2-0.3 mm thickness have been implanted into human organism as part of medical devices. After 9 and 18 years in organism, the implants were taken out of organism and the films have been investigated with the following methods: infrared spectroscopy, X-ray fluorescence analysis, optical microscopy, atomic force microscopy, energy-dispersive spectroscopy, the mechanical tests have been performed.

The results showed that the mechanical strength increases with time in organism in comparison with control film on air. The surface layer is calcified, the thickness, uniformity and composition of the calcified layer depends on time in organism and individuality of the organism.

Keywords: *Polyurethane films, investigated, biocompatible*

The study was supported by Ministry of Education of Perm Region on the program "International research group". Agreement C-26/632 from 19.12.2012.

Titania sol-gel coating with silver on non-porous titanium and titanium alloys

Diana Horkavcová¹, Martin Černý¹, Ludvík Šanda¹, Pavel Novák², Eva Jablonská³, Aleš Helebrant¹
diana.horkavcova@vscht.cz

¹Department of Glass and Ceramics, Faculty of Chemical Technology,
Institute of Chemical Technology Prague, Czech Republic

²Department of Metals and Corrosion Engineering, Faculty of Chemical Technology,
Institute of Chemical Technology Prague, Czech Republic

³Department of Biochemistry and Microbiology, Faculty of Food and Biochemical Technology,
Institute of Chemical Technology Prague, Czech Republic

The objective of the work was to prepare and characterize titania sol-gel coatings on non-porous titanium and titanium alloys. Titanium substrates (Ti, TiSi5, TiSi10) were mechanically treated. Basic titania sol contained two forms of silver (AgNO₃, Ag₃PO₄). Titania sol without silver was used as a reference sample. Coatings were prepared by dip-coating technique during stirring and fired at 400°C.

Coatings after firing were characterized by electron microscopy. All titania coatings were measured to determine their adhesive and bactericidal properties. Adhesion of the coatings to the substrate was measured by tape test (ASTM D 3359-2), where the cut area was evaluated visually by optical microscope. Gram-negative bacteria *E. coli* (strain DBM 3138) was used for the bactericidal test. Coated substrates were immersed into suspension of *E. coli* in physiological solution for a period of 24 and 4 hours at laboratory temperature. Cytotoxicity of the materials was also tested. Coated substrates were leached in MEM growth medium for 1 day at 37°C and the extracts were added to mouse fibroblast (L929 cell line, ATCC[®] CCL-1[™]). The cytotoxicity test (ISO 10993-5) was performed after one day and was based on the metabolic reduction of the soluble tetrazolium salt (WST-1) to a colored formazan.

Keywords: *titania coating, sol-gel method, dip-coating technique, antibacterial properties, adhesion*

Acknowledgement: *This work has been supported by the Technology Agency for the Czech Republic within the project TE01020390 Center for development of modern metallic biomaterials for medicinal implants.*

References

- [1] Diana Horkavcová, Tereza Běloubková, Zuzana Mizerová, Ludvík Šanda, Zuzana Cílová, Markéta Častorálová, Aleš Helebrant: Comparison of sol-gel silicate coatings on Ti substrate, *Ceramic-Silikáty* 56 (4) 314-322 (2012)

A Numerical Investigated of Human Tibia During Gait And Running

Kerem Ün¹, Ahmet Çalık²
acalik@cu.edu.tr

¹Department of Electrical & Electronic, Faculty of Engineering and Architecture, Çukurova University, Adana 01330, Turkey

²Department of Mechanical Engineering, Faculty of Engineering and Architecture, Çukurova University, Adana 01330, Turkey

The objective of the study is to analyze stress-strain distribution on human cortical tibia, which is subjected to torsion during gait and running. A three-dimensional finite element model for human tibia bone is created via three-dimensional reconstruction of Computerized Tomographies (CT) images. The variations of maximum values of von Mises stress and strain are computed at each cross-section along the bone axis under pure torsion. Trabecular bone in the proximal tibia and distal tibia is assumed transversely isotropic and homogeneous. Cortical (compact) bone of the shaft tibia is sliced at six different locations perpendicular to the bone length. Furthermore different orthotropic material properties are assigned to each section . Physiological-like static loading conditions (for gait 20 Nm and for running 30 Nm) and all material properties are taken from literature. The results show that maximum von Mises stress and strain are observed in shaft tibia, 128 mm from distal tibia. von Mises stress and strain magnitudes are 28 MPa and 0.0042; 44 MPa and 0.0065 for running, respectively.

Keywords: *Tibia bone, finite element.*

SANS-Studies of the Ordering of Water-Soluble Metallofullerenes for MR-Imaging in Aqueous Solutions

V.T.Lebedev¹, Gy. Török², Kulvelis Yu.V.¹,
Sedov V.P.¹, Szhogina A.A.¹
vlebedev@pnpi.spb.ru

¹B.P.Konstantinov Petersburg Nuclear Physics Institute, NRC Kurchatov Institute, 188300 Gatchina, St.Petersburg distr., Russia

²Research Institute for Solid State Physics and Optics, Wignal Research Centre for Physics of HAS, POB-49, Budapest, Hungary

A review of recent activity in the field of synthesis and small-angle neutron scattering studies of self-assembly of water soluble derivatives of endofullerenes $Gd@C_{82}$ in aqueous solutions as dependent on their concentration and the addition of salts to regulate pH-factor has been presented. The original endofullerenes $Gd@C_{82}$ were transformed into water soluble form $Gd@C_{82}(OH)_X$ ($X \sim 20-30$) and these hydroxylated fullerenes (fullerenols) with Gadolinium atoms possessing magnetic moment are considered as very perspective substances to be used as highly effective and safety (non toxic) contrasting agents for Magneto-Resonance-Imaging to improve the resolution of this method by an order in magnitude.

However these functional properties are strongly dependent on the processes of self-organization of fullerenols having both magnetic and electric dipole moments the interactions of which stimulates molecular ordering in various forms, e.g. globular and low-dimensional (chain-like) aggregates with a characteristic size of few tens of nanometers.

The dimensions, geometry and masses of fullerenols' aggregates have been analyzed by small-angle neutron scattering and the mechanisms as well as some peculiarities of fullerenols' ordering were established using the formalism of molecular correlation functions to understand subtle features of effects of enhancement of relaxivity of surrounding protons in biological media. The related contrasting abilities of these substances can be used in tomography also in mixtures with empty fullerenols when in magnetic fields the paramagnetic and induced diamagnetic moments of fullerenols $Gd@C_{82}(OH)_X$ and $C_{82}(OH)_X$ may provide a collective strong action on the relaxation rate of protons in tissues.

Keywords: *fullerenes, contrast, tomography, imaging, neutron, scattering, structure, ordering*

Thermoplastic properties productions of synthetic polymers for medical applications

Aleksey Reshetnikov, Anton Kasatkin, Ilya Lukoyanov, Tania Urakova, Leisan Chernova
ant-kasatkin@yandex.ru

Department of Pharmacology, Izhevsk State Medical Academy, 426034 Izhevsk, Russia

The study of effect temperature and acidity of medicinal agents to change the elastic properties of intravascular catheters size 18G, made of polyurethane, teflon and silicone. Elastic properties of catheters were determined by measuring the length of the deflection (in mm) arising after exposure to the free end of the tube by force of 20 newtons. Measuring the deflection of the catheter tube was performed under the conditions of incubation for 10 minutes at +25.0, +30.0, +36.0 or +42.0 °C, before and after 24 hours incubation in solution of medicines with pH from 3.0 to 9.0. During the studies found that the change of temperature change affects, but the change in pH does not change the elasticity of the catheters. Moreover, cooling decreases the elasticity of the catheters, but in different ways, depending on the polymeric materials from which catheters are made. Thus catheters formed of teflon, were more elastic than catheters of polyurethane and silicone in all temperature conditions. In particular, at +42 °C the deflection of teflon catheter was equal $13,7 \pm 0,3$ mm ($P \leq 0,05$, $n = 10$), while the catheters made of polyurethane and silicone - $24,9 \pm 0,4$ mm ($p \leq 0,05$, $n = 10$) and $38,4 \pm 0,3$ (respectively).

Additionally, in experiments on conscious of piglets and clinical observations of patients, it was shown that all modern catheters made of silicone, polyurethane and Teflon, cause damage to the endothelium of veins within a few minutes after their catheterization. Consequently, modern catheters have extremely high hardness and low elasticity both at room temperature and at human body temperature, which is the cause of their high physical aggressiveness. This high hardness and low elasticity of modern vascular catheters is the cause of previously, phlebitis, thrombosis and clogging of the veins and catheters.

To enhance the security of vascular catheters is no alternative of their manufacturing of competitive material, which maintains high hardness at a temperature of +25°C, but deprives it of and accorded high elasticity in a few seconds after increase of temperature up to +37°C. To implement this idea we previously developed a new intravascular catheter [1]. Basic technical solution to this catheter is that it is made from a material that with increasing temperature loses its strength and becomes more elastic. In addition, invented by us catheter allows to implement a completely new technology of enter of medicinal product in vienna. The matter is that our catheter is a dockable nipples. This design catheter allows to constantly move of the working end of a catheter inside the vein. Therefore, the "stream" of a medicinal product is poured from the hole of the catheter, which is constantly moving to and fro within the vein.

Keywords: *cathehers, competitive materials, thechnology processes.*

[1] *Urakov, A.L. et al. Method for ulnar vein catheterisation and multiple-dose intravenous drug introduction. Patent RU 2387465.*

Comparative Study on Histological Analysis of Biodegradable Magnesium and Magnesium Alloys

Dong-Ho Lee¹, Kang-Sik Lee¹, Hyung-Seop Han², Yu-Chan Kim³
osdlee@gmail.com

¹Asna Medical Center, University of Ulsan College of Medicine, Orthopedic Surgery

²Korea Institute of Science and Technology, Center of Biomaterials

³Korea Institute of Science and Technology, Orthopedic Surgery

Recently, there have been significant advances in development of biodegradable magnesium alloys as orthopedic implant materials. The results of various reported studies have shown that the implants made of magnesium alloys degrade in physiological settings while promoting positive new bone growth. However, there are currently no standardized methods available in the literature to reflect on to perform the histological evaluation of the magnesium and the unique corrosive characteristic of magnesium often hinders the accurate observation. The purpose of this study was to evaluate the four most commonly used bone histological staining methods to observe their effectiveness when used on magnesium. The samples of magnesium were stained with different solutions and weight loss was measured to determine the corrosive nature of each solution. In vivo histological evaluation of magnesium implanted on a femoral condyle of New Zealand white rabbits was then performed to validate the preliminary weight loss measurement results. The result from this study provides the most effective staining method for the histological evaluation of newly developed magnesium implants.

Sintering and properties of alumina-magnesia ceramics

Romanenko Kristina, Gerber A, Buyakova S.
ribka.kristina@mail.ru

TPU, Institute of Strength Physics and Materials Science Siberian Branch of Russian Academy of Sciences

It is known that aluminum oxide is the most generally used ceramic material applied as structural, functional and biomaterial. Meanwhile, it is used not only in a high state and but also in a high-porous state. To obtain the required functional properties it is alloyed by various oxides such as FeO, SiO₂, Y₂O₃, MgO and others. What most interested us is the magnasium oxide (MgO), as it is well known that the MgO presence in the ceramics materials causes biological processes activation at the boundary "implant – bone". However, the introduction of MgO into sintered mixture may change technological regimes of ceramics production and as a result to the structure and properties of the material can be changed as well. The aim of this work is to study the influence of the concentration of the injected mixture into the sintered MgO in the amount up to 10 wt. % onto porosity, shrinkage characteristics of the microstructure and mechanical properties of the sintered material.

Alumina powder obtained by calcination of aluminum hydroxide, and finely divided magnesium oxide powder obtained by calcination of magnesite were taken as materials under examinations. The mixtures were prepared by mechanical treatment in a drum mill for 25 hours. The ceramics samples were obtained by powder metallurgy techniques, that is cold pressure at a 13 MPa and subsequent sintering of the compacts in the air at a temperature 16000 °C for 1 hour.

The structure of the ceramic, porosity, shrinkage and mechanical properties are investigated. It is shown that with MgO increasing of the porosity increases in the sintered samples, and the strength falls. Composite oxide is formed at high contents of magnesium oxide.

Changes in the physical properties of orthodontic archwires to use mouthwashes

Dominika Magyar¹, Lilla Nádai², Eszter Bognár², and Gábor Fábán¹
fabian.gabor@dent.semmelweis-univ.hu

¹ Department of Paedodontics and Orthodontics, Semmelweis University, 1085 Budapest Hungary,
² Department of Materials Science and Engineering, Budapest University of Technology and Economics, 1111 Budapest Hungary

Introduction: Scientific research has confirmed that, in moist environment (saliva as electrolyte) galvanic corrosion is formed on the surface of the orthodontic brackets and the archwires. The corrosion reducing the effectivity of the orthodontic treatment. Other research reported the use of mouthwash containing fluoride increases corrosion.

Objective: The aim of our research to examine which mouthwash minimally increases the rate of corrosion, ensuring efficient tooth movement and prevent caries.

Materials and methods: The effects of different fluoride-containing mouthwashes on the various bracket - archwire combinations was examined. The research has investigated with the help of stereo, metal and scanning electron microscopy the formed material errors on the surface of nickel - titanium and titanium - molybdenum orthodontic alloys. With energy dispersive x-ray analysis was determined the samples material composition. In addition, the hardness of orthodontic arches was measured.

Results: During the 3 month study different orthodontic bracket-archwire combination was placed in different mouthwashes and galvanic corrosion was detected. The optical, electron, and atomic force microscopy examination showed that the surface of the samples became more smooth and homogeneous. The results of the microhardness measurements revealed that the hardness of the archwires increased. The energy dispersive x-ray analysis revealed that the zirconium and titanium content increased but the molybdenum and tin content is reduced compared to the control sample material composition.

Conclusions: The studies can help ensure that, the patient use the best mouthwash to the current bracket archwire combination, thereby reducing the risk of caries and minimize the decreasing of the orthodontic treatment efficiency.

Keywords: *biomechanics, orthodontics, archwire, nitinol, corrosion, mouthwash, biomaterial, prevention, dent*

Methodological contribution to the mastery of infectious risk associated with health care activities

Hacene Smadi
h.smadi@hotmail.fr

Université of Batna, Institut Hygiene and Safiiy

The infection associated with health care is a major cause of morbidity and mortality in health establishment. For a dialyzed renal failure, it would be responsible of about 15 % of the deaths. To answer this issue, health establishments use a classical approach, which rests essentially on risk management practices, which enters within the scope of a global analysis of risk management. These practices are built on the anticipation principle; they are based on the identification and the control of the possible risks, of which it is practically impossible to guarantee the exhaustiveness of the risky situations, so it is not possible to leave these anticipation practices at the present time. This is why, for better a control of the infectious risks associated with health care, it is necessary to consolidate more and more this preventive approach and thus to minimize the residual risks. For that purpose an approach is proposed, it is based on a continuous primary prevention strategy, which constitutes a first layer of the protection and is supported by some control and monitoring mechanisms of the critical risks. This approach is illustrated via a real case of study. It is carried out at the hemodialysis center at the teaching hospital, CHU-Batna Algeria.

Keywords: *infectious risk, hemodialysis, VHB, VHC, VIH Bacteremia*

The use of different forms of chemical treatment: their effects on elastic properties of crepe band 100% cotton.

Bachir Chemani¹, Rachid Halfaoui², and Madani Maalem³
chemani_ba@yahoo.fr

^{1,2,3}Department of Engineering Process, University M'Hamed Bougarra of Boumerdes, Boumerdes –
35000- Algeria
Laboratory of Processing and Shaping of Fibrous Materials and Polymers

The crepe band 100% cotton is used in hospital care, it occupies a very important place in the field of medical care. Its manufacturing technology is very delicate and depends on the choice of certain parameters such as warp yarn torsion. The elasticity of the fabric is achieved without the use of any elastic material, chemical, artificial or synthetic expansion and it's capable of creating pressures useful for therapeutic treatments. Before use, the band is subjected to treatments of specific preparation for obtaining certain elasticity, however, during its treatment, there are some regression parameters. The aim of this work is to improve the properties of the fabric through the development of manufacturing technology appropriately.

Keywords: *elastic, cotton, processing, torsion.*

Session 2.

Advanced Materials for Extreme Applications

Effect of mineral additives (natural pozzolana and dune sand) by substitution of cement on the performance and durability of mortars

SAIDI Mohammed¹, SAFI Brahim¹
saidimouh@yahoo.fr

¹ Research Unit: Materials, Processes and Environment (UR/MPE),
University of Bumerdes, Algeria

The objective of our work consists of the study of the substitution effects of clinker by mineral additions such as: natural pozzolana and the sand of dunes finely crushed on the mechanical properties and the durability of the mortars worked out according to various combinations' containing these additions. This will make it possible to select optimal proportions for the cements, most powerful, as well from the mechanical resistance point of view from the durability point of view. The results drawn from this research task confirm that the substitution from 20% to clinker 30% by the additions in binary cement (CPA+PZ) or ternary (CPA+PZ+SD) contributes positively the mechanical resistance of the mortars and resistance to the chemical attacks in various corrosive conditions such as: hydrochloric acid, sulfuric acid and nitric acid.

This study has an economic interest for the cement factories and ecological for the environment. The mechanical strength of the different variants is comparable to those of the CPA. The test results of the weight loss and phenolphthalein shows that the chemical resistance of variants (PZ20) and (PZ20 with SD5) are larger compared to the CPA and other variants. This study shows that adding value by substituting a part of clinker. This substitution can save 20% to 30% of clinker used for the manufacture of cement; this will have a beneficial effect for cement and economically (less energy spent for the clinker burning).

This study contributes to the protection of the environment as to produce one ton of clinker generates about one ton of CO₂ is harmful to the atmosphere. Based on our results we will reduce from 20% to 30% CO₂ gas responsible for the greenhouse effect.

Keywords: *Natural pozzolana, Dune sand, Mortars, Mechanical properties, Durability*

References

- [1] P.S.Mangat and J.Khatib "Influence of flay ash, silica fume and slag on sulphate resistance of concrete" ACI Materials Journal – Vol 92 , pp 587 – 594 -1995
- [2] S. M. Torres, J.H. Sharp, R.N. Swamy, C.J. Lynsdale, S.A. Huntley "Long term durability of Portland-limestone cement mortars exposed to magnesium sulphate attack" Cement & Concrete Composites-N° 25, pp 947-954-2003
- [3] M. O'Farrell, S. Wild and B. B. Sabir " Resistance attack of ground brick-PC mortar. PartI: Sodium Sulphate Solution" Cement and Concrete Research - Vol 29, pp 1781-1790-1999.

Fine Grained Concrete Using in Cold Weather Conditions

Liudmila Alexandrovna Veshniakova
l.a.veshnyakova@gmail.com

Northern (Arctic) Federal University named after M.V. Lomonosov
Institute of Building and Architecture

For the Northwest Territories of Russia there is a typical situation where concrete and reinforced concrete structures are operated in extreme conditions such as low temperatures, exposure to salt and acidic environment. For infrastructure development of the northern territories there is a need to develop and apply materials with special properties (strength, watertightness, corrosion resistance, frost-resistance). There is a need for high quality and strength in building materials. Optimization of building material properties is an empirical process, which can take much time and resources. Here we use a thermodynamic approach as a new method for optimal selection of fine grained concrete. This thermodynamic approach helps us to assess the surface properties of fine grained concrete. The activity of the concrete components is characterized by the free surface energy on the boundary of the phases. This new approach can reduce the time needed for concrete content selection and decrease the associated cost. Previously, in [1, 2] the influence of additives on the properties of dry mix and fine grained concrete has been investigated; the optimal content selection based on mechanical and energetic properties of a dry mix has been designed. Evaluation of properties of concrete using microsilica-based filler materials was performed using the following components: coarse river sand, portland cement and fine river sand as the basis for the highly-dispersed filler making. Average size of the particle was 483±39 nm[3]. Frost-resistance of this fine concrete were conducted at multiple freezing (GOST 10060.0-95, GOST 10060.2-95) under alternating temperatures in the range 24 ±-55 Celsius degree. It has been established that the strength properties of the concrete over 4 cycles of freezing-thawing in an aqueous solution of 5% NaCl (which corresponds to 150 cycles of normal operation of the concrete) is not changed significantly -by 4.5%. Determination of water resistance of concrete samples was carried out in accordance with the requirements of GOST 12730.5-84 by the method of the wet spot. The water pressure (10 MPa) was on the on samples when water infiltration was observed. Determination of the rate of corrosion of concrete performed on samples by the variation of the pH - parameter. To ensure consistency in the reactivity tests of the cylindrical surface of the side surface of the samples protected resistant insulating coating based on epoxy . As an aggressive liquids for concrete water and a solution of 0.1 M HCl (acidic environment that simulates the swamp) were chosen.

The experiment results for samples in an acidic liquid are marked by loss of strength by 20 % in comparison with the unsaturated sample repositories in water - 9.5 %. Studies suggest the following conclusion. Designed fine grained concrete can be recommended for using in cold climate.

References

- [1] Veshnyakova L.A., Aisenstadt A.M. Optimization of particle size distribution for the mixtures applied in the fine grained concrete / Industrial and civil engineering, 2012, №8470;10, p.34-37 2.
- [2] Tutygin A., Frolova M., Aisenshtadt A., Veshnyakova L.. Determination of free surface energy of nano-dispersed materials. - 18. Internationale Baustofftagung (18. ibausil), Beton und Betondauerhaftigkeit Durability of Concrete, Weimar,12-14.09.2012, P 2.24., p. 2-0636 - 2-0643

Characterization of Ball-Milled Carbon Nanotube Dispersed Aluminium Mixed Powders

Md Abdul Maleque¹, Umma Abdullah¹, Iskandar Idris Yaacob¹, Mohammed Yeackub Ali¹
maleque@iium.edu.my

¹Department of Manufacturing and Materials Engineering
Kulliyah of Engineering, International Islamic University, Malaysia
P.O.Box 10, 50728 Kuala Lumpur, Malaysia

Currently, carbon nanotube (CNT) is attracting much interest as fibrous materials for reinforcing aluminium matrix composites due to unique properties such as high strength, elastic modulus, flexibility and high aspect ratios. However, the quality of the dispersion is the major concern factor which determines the homogeneity of the enhanced mechanical and tribological properties of the composite. This work study and characterized carbon nanotube dispersion in ball-milled CNT-aluminium mixed powders with four different formulations such as 1, 1.5, 2 and 2.5 wt% CNT under high energy planetary ball milling operations. The ball milling was performed for two hours at constant milling speed of 250 rpm under controlled atmosphere. The characterization is performed using FESEM and EDX analyser for mapping, elemental and line analysis. The experimental results showed homogeneous dispersion of CNTs in aluminium matrix. The compositions of 1.5, 2 and 2.5 wt% CNT dispersed CNT-Al composite mixture showed similar pattern from mapping, elemental and line analysis. Identification of only two peaks proved that control atmosphere during milling prevented the formation of inter metallic compounds such as aluminium carbide in the composite mixture. Therefore, this CNT-Al composite powder mixture can be used for new nano-composite development without any agglomeration problem.

Keywords: Carbon nano tube, Aluminium powder, Dispersion, FESEM

Reaction sintering as borurization in B₄C composites

Mauro Mazzocchi, Luca Zoli, Daniele Dalle Fabbriche, Diletta Sciti
luca.zoli@istec.cnr.it

Institute for Science and Technology of Ceramics-Italian National Council of Research, Faenza, Italy.

Boron carbide is an interesting non oxide-covalent material, with a remarkable stiffness (450GPa), extremely high hardness, wear properties and a low density that make it very attractive for specific applications. B₄C has found almost exclusively special applications further the elective one as abrasive: as peculiar lightweight ceramic armor material and has been used for nuclear engineering for its neutron absorption ability and properties of structural self-healing rearrangement. Despite these interesting properties, B₄C sintering is difficult due to its highly covalent character: densification is achieved by Hot Pressing technology and/or conventional sintering at temperatures exceeding 2000°C and addition of sintering aids that form secondary phases (C, SiC, borides, silicides, etc.) detrimental to mechanical performances.

In this work, attempts to achieve higher densities and improved performance were conceived by combining B₄C with ZrB₂, that possesses high hardness, high modulus and extremely high melting point exceeding 3000°C. The composites were produced by in situ reactive sintering following different approaches for borurization of Zr: a solid-solid route, through blending of suitable powders, or liquid-solid one, by introducing solvated ionic Zr into the microstructure or around B₄C grains. A resistance graphite furnace for pressureless sintering and a unique hot pressing device with an induction furnace equipment capable of extreme high heating rates (>8000°C/h) was used for sintering tests; an HP fast ramp in heating followed by a fast cooling -allowed by the furnace engineering- was set to inhibit grain growth. Microstructural SEM characterization and some mechanical performances were carried out to evaluate the obtained B₄C-ZrB₂ composite materials.

Keywords: *carbonium boride, zirconium boride, covalent materials, composite, reaction sintering, armor materials*

Diffusive-Hardening Alloys Cu-Bi-Ga-In-Sn: Structure and Thermal Properties

Alexey Shubin¹, Konstantin Shunyaev¹, Viktor Bykov¹
abshubin@gmail.com

¹Institute of Metallurgy, Urals Branch of RAS.
101 Amundsena St., Ekaterinburg, 6200016, Russian Federation.

Diffusive-hardening solders based on gallium don't contain lead. These alloys demonstrate specific rheological properties. Their synthesis includes, as a rule, mechanical mixing of such an initial components as metallic powders (fillers) and liquid gallium alloys. Further the metallic pastes produced show irreversible phase transformations and form the solid alloy with complicate composite structure. Here, we investigated the microstructure and some thermal properties of the diffusive-hardening alloys Cu-Bi-Ga-In-Sn. These studies were performed by the standard SEM, EDX and XRD methods and also using differential scanning calorimeter.

The alloys produced as a result of a "cold" solidification of the Cu-Bi-Ga-In-Sn pastes are metastable and include more than two phases. Nevertheless technological characteristics of such an alloys are high. They can be applied, in particular, to create comparatively durable and vacuum-tight joints of metallic and non-metallic materials.

Thermal properties of the solidified alloys were determined mainly by their complicate structure. As a rule the samples contained residuals of initial filler particles (e.g. Cu-Sn alloy), crystal phases like CuGa₂, InBi and other comparatively fusible phases (e.g. solid solution of gallium in the tin and indium). In such non-equilibrium system of complicate composition the interaction of components begins again after heating to the temperatures about 100 °C and higher.

DSC endothermic peaks obviously correspond to the fusible phases melting, then melting or decomposition of the intermetallic phases detected. Further heating leads to another phase transformations and at last to the real melting of the metallic phase. Then the composite multi-phase alloy turns into ordinary multi-component system which can be described using equilibrium thermal and thermodynamic approaches.

The diffusive-hardening alloys and their analogues are widely used as the metallic glues, solders and dental materials. Our systematic investigations of structural, mechanical and thermal properties of the gallium-containing materials were continued in the present work.

This work was supported by the Program of the Presidium of Russian Academy of Sciences (Project 12-P-3-1032).

Keywords: *gallium, copper, indium, tin, bismuth, alloy, structure, thermal properties.*

Liquid marbles prepared via external stimuli-responsive particles

Shin-ichi Yusa¹, Keita Nakai¹, Masashi Morihara¹, Hinari Nakagawa¹,
Keita Kuroda¹, Yoshinobu Nakamura² and Syuji Fujii²
yusa@eng.u-hyogo.ac.jp

¹ Department of Materials Science and Chemistry, University of Hyogo,
2167 Shosha, Himeji, Hyogo 671-2280, Japan

² Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology,
5-16-1 Ohmiya, Asahi-ku, Osaka 535-8585, Japan

Recently, there has been an increasing interest in solid particles adsorbed to liquid-liquid, gas-liquid and gas-solid interfaces. Liquid marbles are liquid-in-gas dispersed systems prepared using hydrophobic particles adsorbed to a gas-liquid interface. They have attracted increasing attention with respect to their potential applications in cosmetics, pharmaceuticals in the home, and personal care products. The liquid marbles which are coated with hydrophobic particles can float on a water surface. Various particles have been used to prepare liquid marbles, including surface-modified silica, graphite, synthetic polymer particles, and carbon black powder. Liquid marbles have demonstrated potential as micro-reactors, micro-pumps, sensors of gas, and water pollution, in addition, possible applications in cosmetics and water storage are of considerable industrial interest. For liquid marbles to be utilized as delivery systems, it would be desirable for them to release the guest materials by various external stimuli [1-7].

In this study, to obtain near-infrared (NIR)-responsive liquid marbles, we prepared liquid marbles using carbon nanotube (CNT) and fullerene (C₆₀), which are known to have high absorbance in the NIR region. It was possible to prepare liquid marbles from the CNT and C₆₀ powders due to the hydrophobic nature of them. The preparation method was as follows. First, the CNT or C₆₀ powder bed was prepared. A water drop was deposited on the powder bed. Upon gentle rolling of the water droplet on the powder bed, the liquid became entirely encapsulated by the powder, resulting in a liquid marble.

Keywords: *stimuli-responsive, polymer, interface, powder*

References

- [1] D. Dupin, S.P. Armes, S. Fujii, J. Am. Chem. Soc. 131 (2009) 5386.
- [2] S. Fujii, S. Kameyama, S.P. Armes, D. Dupin, M. Suzuki, Y. Nakamura, Soft Matter 6 (2010) 635.
- [3] S. Fujii, M. Suzuki, S.P. Armes, D. Dupin, S. Hamasaki, K. Aono, Y. Nakamura, Langmuir 27 (2011) 8067.
- [4] K. Nakai, H. Nakagawa, K. Kuroda, S. Fujii, Y. Nakamura, S. Yusa, Chem. Lett. 42 (2013) 719.
- [5] K. Nakai, S. Fujii, Y. Nakamura, S. Yusa, Chem. Lett. 42 (2013) 586.
- [6] M. Inoue, S. Fujii, Y. Nakamura, Y. Iwasaki, S. Yusa, Polym. J. 43 (2011) 778.
- [7] S. Yusa, M. Morihara, K. Nakai, S. Fujii, Y. Nakamura, A. Maruyama, N. Shimada, Polym. J. in press, doi:10.1038/pj.2013.84.

Degradation of Ceramic Matrix Composites under mechanical loading: modeling and experiments

Tomasz Sadowski, Daniel Pietras
t.sadowski@pollub.pl

¹Department of Solid Mechanics, Lublin University of Technology, Lublin 20-618, Poland

Modern Ceramic Matrix Composites (CMCs, e.g. $\text{Al}_2\text{O}_3/\text{ZrO}_2$) have a non-linear and complex overall response to applied loads due to: different phases, existence of an initial porosity and internal microdefects. All microdefects act as stress concentrators and locally change the state of stress, leading to the development of mesocracks and finally macrocracks. Experimental results show that defects develop mainly intergranularly and cause inhomogeneity and induced anisotropy of the solid. Modelling of such material response is possible by multiscale approach describing different phenomena occurring at different scales:

- the microscopic level is associated with the degradation phenomena developing at the single grain. Micropores inside of grain or at the grain boundaries act as a crack initiators. Microcracks spread along grain boundaries,
- the mesoscopic level corresponds to a set of grains, which create Representative Surface Element (RSE). The basic elements of the defect structure are: meso-cracks, which diameters correspond to the single straight facet of the grain boundaries structure, kinked and wing (zig-zag) cracks,
- the macroscopic level corresponds to the dimensions of the tested sample of the material. The composite is treated as a continuum with properties of the polycrystal calculated as averaged values over of RSE.

The constitutive equations for the considered CMC are the following:

$$\varepsilon_{ij} = S_{ijkl}(\sigma_{mn}, p, \omega^{(i)})\sigma_{kl}$$

where S_{ijkl} is the compliance tensor, ε_{ij} is the strain tensor, σ_{kl} is the stress tensor, p is the porosity parameter and $\omega^{(i)}$ are sets of parameters defining the presence of different kinds of defects "i" developing inside the material.

The model was verified by experiments under quasi-static loading. The obtained results confirm the correctness of the theoretical approach.

Keywords: *degradation process, modelling of CMC, experimental verification*

Acknowledgement Financial support of Structural Funds in the Operational Programme - Innovative Economy (IE OP) financed from the European Regional Development Fund - Project "Modern material technologies in aerospace industry", No POIG.0101.02-00-015/08 is gratefully acknowledged (RT-10: Modern barrier covers on critical engine parts).

Zirconia – alumina porous ceramic produced by using aluminum hydroxide

I. Zhukov, S. Buyakova, V. Promakhov, E. Kalatur, S. Kulkov.
gofra930@gmail.com

Institute of Strength Physics and Materials Science SB RAS
634021, Russia, Tomsk.

Porous composites $ZrO_2 - Al_2O_3$ have physical - mechanical properties such as high strength, high fracture toughness, resistance to aggressive media. These composites are widely used as a material for manufacturing the membranes, for catalysts, implants, refractories.

In this paper the effect of a process for producing powders of zirconia and aluminum hydroxide , their ratio in the powder mixture, sintering temperature and porosity in composites $ZrO_2 - Al_2O_3$ has been studied. It has been shown that increasing of the sintering temperature from 1500 to 1600 °C for zirconia powder produced by chemical vapor deposition is not accompanied by an increase of its density. It was found that in composites $ZrO_2 - Al_2O_3$ the concentration of the tetragonal phase determines the size of its crystallites: at low contents by tetragonal - monoclinic transformation, and at large by recrystallization. The crystallite size of the tetragonal zirconia determined by the porosity of the sintered material. It was found that the strength of materials $ZrO_2 - Al_2O_3$ with zirconia powder obtained by plasma-chemical method is higher when strength of composites with powder obtained by chemical vapor deposition, and does not depend on the type of aluminum hydroxide powder in the initial mixture.

Keywords: *Zirconia, hydroxide aluminium, composites, porosity.*

Financial support by Grant President RF MK - 5681.2014.8; MK - 5883.2014.8. RFBR grant HK 14-08-31087\14.

Structural transitions and magnetic properties of orthorhombic fluorite-related compounds Ln_3MO_7 (Ln = rare earths, M = transition metals)

Yukio Hinatsu¹, Yoshihiro Doi¹, and Makoto Wakeshima¹
hinatsu@sci.hokudai.ac.jp

¹Department of Chemistry, Hokkaido University, Sapporo 060-0810, Japan

We report structural transitions and magnetic properties of ternary metal oxides with general formula Ln_3MO_7 (Ln is a rare earth element; M is a pentavalent transition element such as Mo, Ru, Re, Os, or Ir) by the high temperature X-ray diffraction, magnetic susceptibility, specific heat, and DSC measurements. These compounds have an ordered, defect-fluorite structure. The relationship to the fluorite structure is as follows. The fluorite unit cell for oxides has the composition $M^{4+}_4O_8$. If the four tetravalent metal ions are replaced by three trivalent ions (Ln) and one pentavalent ion (M), one oxide vacancy is formed per fluorite cell. Due to significant differences in radii between the Ln^{3+} and M^{5+} ions, cation ordering occurs on the metal sites and the oxide-vacancy orders on the anion sites. These compounds crystallize in an orthorhombic superstructure of cubic fluorite with space group $Cmcm$, in which Ln^{3+} ions occupy two different crystallographic sites (8-coordinated and 7-coordinated sites).

A variety of space groups such as $Pnma$, $Cmcm$, $P2_12_12_1$, $C222_1$, $P2/n$ and $P2_1nb$ have been proposed for the Ln_3MO_7 . We confirmed that these compounds undergo a structural phase transition. For a series of Ln_3MO_7 compounds ($M = Mo, Ru, Re, Os, Ir$), the structural phase transition temperatures decrease greatly with increasing the ionic radius of Ln^{3+} . Since the transition temperature increases with decreasing the ionic radius of Ln^{3+} , this transition is stress-induced and it occurs with lattice contraction on cooling. Each transition temperature within a series is separated by approximately the same temperature interval except for the case of Ln_3MoO_7 . The reason for this may be related to the difference in their high-temperature structures, that is, Ln_3MO_7 ($M = Ru, Re, Os, Ir$) compounds exist in the $Cmcm$ structure, whereas Ln_3MoO_7 exists in the $Pnma$ structure.

In Ln_3MO_7 structure, the M^{5+} ion is coordinated with six oxygen ions, forming a MO_6 octahedron. These octahedra share corners forming one-dimensional chains which are oriented along the c -axis. Due to this unique crystal structure, many peculiar magnetic properties have been observed at low temperatures. Recent results on Pr_3OsO_7 and Tb_3OsO_7 by the specific heat and magnetic susceptibility measurements will be reported.

Keywords: structural transition, magnetic properties, rare earth, high temperature X-ray diffraction, magnetic susceptibility, specific heat

Properties of ZrO₂ - TiC dispersion reinforced composite materials

Grigoriev M.V.^{1,2}, Buyakova S.P.^{1,2,3}, Kul'kov S.N.^{1,2,3}
grv@ispms.tsc.ru,

¹Institute of Strength Physics and Materials Science of Siberian Branch Russian Academy of Sciences, 634021, Russia, Tomsk

²National Research Tomsk Polytechnic University, 634050, Russia, Tomsk

³National Research Tomsk State University, 634050, Russia, Tomsk

Stabilized zirconia polycrystals, as tetragonal polymorph, have an outstanding bending strength (>1000 MPa) and fracture toughness (>10 MPa*m^{1/2}). These materials have a not enough hardness (<1200 kg/mm²) limiting their use as wear resistant components. On the other hand, pure carbide inclusions have an excellent hardness, but a limited bending strength, fracture toughness and stiffness. The degree of improvement is in different ZrO₂-TiX (X =C, B2, N, CN) composite systems. To combine the excellent properties of stabilized zirconia with the increased hardness obtainable by incorporation of a secondary phase such as TiC was the main objective of this work.

Maximum of density after sintering can be achieved by means of separate ball-milling activation of powders, as compare with the its mixtures. It was shown that addition of 5wt.% TiC, provides a minimum porosity of about 1% and a maximum hardness of 12.5 GPa.

Structure of composites represented by two types of zirconia grains - small order of 1-2 microns, and large order of 5 microns, and titanium carbide grains whose size is 15 microns. Isolated pores are present on the grain junctions in the form close to spherical, the dimensions of which do not exceed 2 μm. A distinctive feature of the structure of ceramic composites ZrO₂(Y₂O₃)-TiC is the formation of abnormally large grains of zirconia around titanium carbide inclusions. Conducted in the field of elemental analysis showed the presence of a large grain of chemical elements characteristic for all elements of the composition. Accordingly, it can be assumed in the interfaces between the titanium carbide and zirconia one can observed a reaction with formation of oxide-carbide compounds.

Keywords: *ceramic, composite materials, titanium carbide, hardness, structures*

Development of piezoelectric ceramics for high temperature applications

E.D. Politova¹, G.M. Kaleva¹, A.V. Mosunov¹, V.S. Akinfiev², S.Yu. Stefanovich^{1,2}, A.H. Segalla³
politova@cc.nifhi.ac.ru

¹*L. Ya. Karpov Institute of Physical Chemistry
Obukha s.-st., 3-1/12, b.6, 105064, Moscow, Russia*

²*Faculty of Materials Science, Lomonosov Moscow State University,
Leninskie gory, 1, Moscow, 119992, Russia,*

³*ELPA Company,
Panfilovsky pr. 10, Zelenograd, 124460, Moscow, Russia*

Strong demands of various industries simulated search for new piezoelectric materials for high temperature applications. To improve sintering and regulate functional properties, various approaches were used, however, till now functional properties of new perovskite-type materials do not compete with those of the PZT-based materials.

In this work, structure, microstructure, dielectric and piezoelectric properties of oxides based on the $(1-x)\text{BiScO}_3 - x\text{PbTiO}_3$ (BSPT) with $x = 0.63 - 0.65$, and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ compositions close to the Morphotropic Phase Boundary were studied. In order to regulate functional properties, modification of cation compositions, addition of overstoichiometric additives (MnO_2 , chlorides KCl , NaCl , CaCl_2 and fluoride LiF) and optimization of preparation conditions were performed. The samples were prepared by the solid state reaction method. Phase formation, structure parameters and functional properties were studied using the X-ray diffraction, SEM, SHG, and Dielectric Spectroscopy methods. Piezoelectric parameters d_{33} and k_t of the preliminary poled samples were measured.

Optimal sintering conditions of dense and textured ceramics preparation were determined. The variations of relative contents of tetragonal and rhombohedral phases, structure and microstructure parameters, dielectric and piezoelectric properties were observed depending on composition and thermal treatment conditions. The 1st order phase transitions were observed for all samples at high temperatures $\sim 700 - 1000$ K. The changes of the T_C values correlated with the changes in the unit cell parameters and relative phase content caused by doping. High piezoelectric coefficients d_{33} up to ~ 500 pC/N and $k_t \sim 0.65$ values were measured in the BSPT ceramics prepared. Enhancement of piezoelectric properties will be discussed in relation to the preparation conditions, type and content of dopants.

Keywords: *piezoelectric ceramics, perovskite oxide, overstoichiometric*

Low thermal expansion NZP ceramics

Vladimir Pet'kov, Elena Asabina, Igor Schelokov, Aleksandr Shipilov,
Irina Glukhova, Vasily Shatunov, Artem Alekseev, Ivan Korchemkin
ikorchemkin@gmail.com

Lobachevsky State University of Nizhni Novgorod, 603950 Nizhni Novgorod, Russia

One of the important properties of materials for many technological and practical applications is thermal expansion. From the technological point of view, low thermal expansion materials (their absolute value of coefficient of thermal expansion $\alpha < 2 \cdot 10^{-6} \text{K}^{-1}$) are the most important ones. The thermal expansion of the compounds of kosnarite ($\text{KZr}_2(\text{PO}_4)_3$) structural family (also known as $\text{NaZr}_2(\text{PO}_4)_3$, NZP, NASICON) change from strongly positive to nearly zero and even negative [1, 2]. The NZP structure allows a huge variety of ion substitutions not only to the framework cavities but also to the rigid framework. A variety of solid solutions with the NZP structure leads to new candidates for compositions with totally controllable low-expansion behavior.

Basing on data on thermal expansion behavior of the complex phosphates of titanium (zirconium) and metals in oxidation state 2+, we undertook systematic search for materials with ultra-low average thermal expansion and near-zero thermal expansion anisotropy. We studied phase formation and thermal expansion of the phosphates $\text{B}'_{0.5+x}\text{B}_x\text{L}_{2-x}(\text{PO}_4)_3$ (B' and B – the same or different cations in oxidation state 2+ (Ca, Mn, Co, Zn), L – Ti, Zr), $\text{B}_{0.5(1+x)}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (B – Mn, Co, Ni, Cu, Zn), $\text{AZr}_2(\text{TO}_4)_x(\text{PO}_4)_{3-x}$ (A – alkali metals, T – As, V). As a result, correlations of the thermal expansion parameters on the phosphates composition were obtained in the studied systems. Basing on these regularities, we predicted and obtained compounds with desired thermal expansion characteristics. In some investigated systems, the extremely low values of thermal expansion coefficients ($\alpha_{av} \sim 1 \cdot 10^{-6} \text{K}^{-1}$) or anisotropy ($|\alpha_a - \alpha_c| < 1 \cdot 10^{-6} \text{K}^{-1}$) were obtained.

This work was made using equipment Shimadzu Corp.

The work was supported by the Russian Scientific Foundation.

Keywords: *ceramics, NZP, kosnarite structure, low thermal expansion.*

References

- [1] V. I. Pet'kov, E. A. Asabina. Thermophysical Properties of NZP Ceramics (A Review) // Glass and Ceramics. 2004. V. 61. № 7-8. P. 233-239.
- [2] Vladimir I Pet'kov. Complex phosphates formed by metal cations in oxidation states I and IV // Russian Chemical Reviews. 2012. V. 81. № 7. P. 606-637.

Tridymite- and maricite-type phosphate ceramics as materials for nuclear storage matrix

Korchemkin Ivan, Pet'kov V.I.
ikorchemkin@gmail.com

Lobachevsky State University of Nizhni Novgorod, 603950 Nizhni Novgorod, Russia

The complex phosphates with high cesium concentration of the compositions CsMePO_4 (Me = divalent metal with a tetrahedral coordination) adopting a stuffed $\beta\text{-SiO}_2$ tridymite structure are studied as perspective ferroelectric, non-linear optical materials and ceramics for a ^{137}Cs γ -radiation sources to be used in commercial and medical applications.

In this work we have studied phase formation regularities and thermophysical properties of phosphates system CsMPO_4 (M = Co, Mn), $\text{Cs}_{1-x}\text{Na}_x\text{NiPO}_4$ ($0 \leq x \leq 1$).

The samples were synthesized by the co-precipitation method. The reaction mixtures were dried at 353 K and thermally treated at 873 and 973 K.

X-ray powder diffraction measurements indicated that limited solid solutions in $\text{Cs}_{1-x}\text{Na}_x\text{NiPO}_4$ system of the tridymite and maricite structural types were obtained. The samples of CsMnPO_4 and CsCoPO_4 were crystallized at ambient temperature in tridymite structural type. The samples were investigated by DTA method over the temperature range 298–1273 K.

Crystal structure of CsNiPO_4 and NaNiPO_4 were refined by Rietveld method at 298 K. CsNiPO_4 crystal structure is characterized by three-dimensional framework, which is formed six-membered rings of tetrahedra NiO_4 and PO_4 , linked by common vertices, and by large cavities that are occupied by Cs cations. NaNiPO_4 crystal structure consists of edge-sharing chains of NiO_6 octahedra running parallel to the b axis, which are crossconnected by the PO_4 tetrahedra, giving rise to large ten-coordinate cavities in which the Na ions are located.

The heat capacity measurements of CsMnPO_4 and CsCoPO_4 crystalline phosphates were performed over the temperature range 5–650 K. The temperature dependence of the heat capacity of crystalline CsMnPO_4 showed that for the phosphate two phase transitions were found at 6.86 K and 126.99 K. The temperature dependence of the heat capacity of crystalline CsCoPO_4 showed that for the phosphate three phase transitions were found at 311, 481 and 512 K.

The thermal expansion behavior of CsMPO_4 (M = Ni, Co, Mn) and NaNiPO_4 was studied by high-temperature X-ray powder diffraction at the temperature range 298–973 K. The samples expand anisotropically and belong to high-thermal expansion materials. The prepared ceramics showed a volume thermal expansion coefficient of $(3\div 7) \cdot 10^{-5} \text{ K}^{-1}$.

The high specific content of the cesium in β -tridymite structure some phosphates in combination with thermal and hydrolytic stability account for the prospects for their using as safe ceramic materials for cesium γ -radiation sources.

This work was made using equipment Shimadzu Corp.

Keywords: phosphate, cesium, structure, tridymite, maricite, heat capacity, ceramic, nuclear waste

Structure and some properties of modified spark plasma sintered (SPS) mullite –ZrO₂ ceramics

G.Sedmale, I.Sperberga, I.Steins, L.Grāse
gsedmale@ktf.rtu.lv

Riga Technical University
Institute of Silicate Materials

The objective of this work is to evaluate SPS sintering for obtaining of high strength mullite - zirconia ceramics. To highlight the advantage of SPS processing over conventional reaction sintering there is compared densification behaviour, phase and structure development and some properties. To promote and lower the sintering process and temperature the effect of illite clay nanoparticles on densification of mullite – ZrO₂ ceramic to one part of starting composition was used.

Conventional sintering was realized in air at max temperatures from 1200 to 1400 °C, for the SPS the “Sumimoto, Model SPS – 825.CE, Dr. Sinter, Japan” equipment was used. Microstructure and phase composition of sintered samples was analysed using SEM (model JSM-T200, Japan) and XRD (model Rigaku, Japan, with CuK_α radiation at scanning interval from 2θ = 10-60 ° and speed 4 °/min), respectively.

The compressive strength was determined by Toni-technic (Baustoffprüfung) model 2020, Vicker's microhardness HV_s, by equipment 2137 TU- UHL 4.2.

It is shown that formation of mullite starts at an SPS temperature of 1150⁰C and completes at designate temperature 1250⁰C, whereas by conventionally sintering weakly start at 1200⁰C and develop until 1400⁰C. It is shown that by both sintering techniques ZrO₂ transform into more stable forms – partly in ZrO₂ tetragonal by conventional sintering and ZrO₂ cubic by SPS. Effect of illite additive is effective on density and compressive strength increase only for conventionally sintered samples, but not for SPS.

Effect of acid activation and pillared on physico-chemical, textural and rheologic properties of montmorillonite used as facial mask

O. Ngomo^{1,2}, J. M. Sieliechi¹, J.B. Tchatchueng¹, R. Kamga¹, A. Tabacaru⁴, R. Dinica³, M. Praisler³
orleansn@yahoo.fr

¹Department of Applied Chemistry, National School of Agro-Industrial Sciences, University of Ngaoundere, BP.455 Cameroon.

²Department of Chemistry, Faculty of Sciences, University of Yaounde I, BP. 812 Cameroon.

³Department of Chemistry, Physics and Environment, Faculty of Sciences and Environment, "Dunarea de Jos" University of Galati, Galati, 800008, Romania.

⁴Department of Chemical Sciences, University degli Stuti of Camerino, Via S. Agostino 1, 62032 Italy.

In order to improve the surface properties of the material to make it more effective, montmorillonites from Maroua in the far north region of Cameroon have undergone activation by 0.5 M hydrochloric acid and pillared with solution of AlCl_3 . To this aim, the determination of structural, textural and rheological properties were made on these modified clays by using techniques as SEM, EDX, FTIR, XRD, TGA, BET and using a rheometer. It appears from these analyzes that the acid activated clays show a reduction in particle size that can means the destruction of the crystalline structure. The pillared clays show densification of materials witch corresponding to insertion of polycations within the leaf. The chemical composition reveals the presence of important cations such as magnesium (0.711 and 0.284%), Sodium (0.112 and 1.491%). Montmorillonite pillared lost approximately 40% of the initial proportion of aluminum, which promotes its cosmetic applications. The activated montmorillonites have a surface area of $116.86 \text{ m}^2/\text{g}$ with a total pore volume of 129 ml/g , montmorillonites pillared have a surface area of $108,32 \text{ m}^2/\text{g}$ with a total pore volume of 0.116 ml/g . According to the rheological analysis, both viscosity decreases with shear rate, karakteristic of pseudoplastic. It is therefore observed for montmorillonites pillared a better resistance to cracking and good thixotropy, excellent for facial mask.

Keywords: *pillared and acid activated montmorillonite, structural, textural and rheologic properties, facial mask*

Heat resistant ceramics based on ZrO₂-MgO

V. Promakhov, S. Buyakova, I. Zhukov, E. Kalatur, S. Kulkov
vvpromakhov@mail.ru

Institute of Strength Physics and Materials Science SB RAS, 634021, Russia, Tomsk
National Research Tomsk State University, 634050, Lenin Pr. 36, Russia, Tomsk
National Research Tomsk Polytechnic University, 634050, Lenin Pr. 30, Russia, Tomsk

Ceramic materials based on zirconia have a high melting point and physical - mechanical properties. These composites can be used as a thermal barrier structures. It is known that the introduction of magnesium oxide to zirconia ceramic can improve the thermal stability of materials because microstructure of such materials can be controlled by relative content of the phases.

In this paper were studied structure and mechanical properties of ceramic ZrO₂ - MgO with various magnesium oxide content. It was shown that under thermal-shock cyclic one can observed the evolution of the structure and phase composition of the material. It has been shown that decreasing in of the content t-ZrO₂ up to 10 % does not lead to the destruction of material. In the process of thermal cycling there are formed a stable cracked block structure, while the strength of ceramics was more than 100 MPa i.e. such thermomechanical stability under thermal cyclic alloweds to create a durable thermal protection material.

Keywords: *zirconia, magnesia, heat resistant, mechanical properties.*

Financial support by Grant President RF MK - 5681.2014.8; MK - 5883.2014.8. RFBR grant HK 14-08-31087\14.

Plasma Torch with Pyrolytic Graphite Electrode

Alexandr Ustimenko¹, Vladimir Messerle¹, Valeriy Lukyachshenko¹,
Kuanish Umbetkaliev², Victor Shevchenko¹
ust@physics.kz

¹Combustion problems Institute, Plasmatechnics
²Combustion problems Institute, Plasmochemistry
Bogenbai Batyr 172 Almaty, Kazakhstan

There are plasma torches of linear circuits, containing coaxially mounted copper electrodes: a cylindrical cathode and an anode having an outlet nozzle in the form of a diffuser. The purpose of these plasma torches is to generate air plasma with outlet temperature from 3500 up to 5500 K, and use it for heavy fuel oil or gasless start up of pulverized coal fired boilers of thermal power plants. The main feature of the plasma torch with pyrolytic graphite electrode is the presence of the insert molded into a cylindrical copper cathode. Hydrocarbon gas is injected in the region of the face plane of cylindrical graphite insert. Its rate is of two orders smaller than the rate of plasma gas flow - air. In the electric arc hydrocarbon gas is dissociated and thus the resulting carbon deposited on the end face of the graphite insert of the cathode spot. Investigation showed that this carbon deposit is a nanostructural material. As a result, a revolving pyrolytic graphite cathode layer prolongs life of the cathode several times.

The determination of angular velocity of the die in pultrusion of a composite anisotropic rod

Sergey Grigoriev¹, Andrey Kutin², Aleksandr Krasnovskii³, and Ilya Kazakov⁴
al.krasnov@mail.ru

¹⁻² Moscow State Technological University "STANKIN", 127055 Moscow, Russia
³⁻⁴ Department of Composite materials, MSTU "STANKIN", 127055 Moscow, Russia

Products from polymeric composite materials, in particular, the rods of circular cross section are widely used as construction valves, electrical insulators and pump rods, pit-prop anchors in the mining industry, and area of their application is constantly expanding. The most widely used unidirectionally reinforced fiberglass rods with a diameter of 2 to 46 mm with high volume content of glass reinforcing fibers 0.60-0.75, produced by pultrusion. The epoxy resin is used as a matrix, and the fiberglass with a filament diameter of 13 to 20 microns used as filler. These rods have a high tensile strength in the longitudinal direction and weak in compression and torsion in the transverse direction. Traditional pultrusion technology allows producing axisymmetric composite profiles only with "zero" fiber orientation angle. The authors of this article developed a special technological complex for the polymer composite materials manufacturing [Patent Rus № 122606, B29C 70/30, B29C 63/04, 2012] which allows orienting fibers on a screw line during production. In this case, the composite rod becomes anisotropic, and its strength characteristics in compression and torsion increases with some decrease of tensile strength. By varying the angle of fiber orientation relative to the pultrusion direction during its manufacture can obtain products with predetermined properties, the most appropriate to operating conditions. This favorably distinguishes these products from composite rods with longitudinal orientation of the reinforcing fibers.

The equations of structural mechanics were used, as well as specific approach to determine the shear modulus of the heterogeneous Fiber/Resin System. As result of this, equations for fiber orientation angle of a composite anisotropic solid rod with a circular cross section and angular velocity of the die were obtained. The results will be applied to die design.

Keywords: *pultrusion, composite material, rotating die, anisotropic rod, pit-prop anchor*

Experimental and Numerical Investigations on Adhesively Bonded Joints

Negru Radu¹, Marsavina Liviu¹, and Hluscu Mihai¹
blackradu@yahoo.com

¹Department of Mechanics and Strength of Materials, University Politehnica Timisoara, Timisoara, Victoriei Square no.2, 300006, Romania

Adhesively bonded joints are used in many engineering applications (automotive and aerospace industries) as an alternative to the conventional riveted and bolted joints. Several advantages characterize the adhesive bonding, including: good stiffness and strength, reduced weight and cost, capacity to join dissimilar materials. Delicate joining technology (surface preparation, curing procedure etc.) and environmental sensitivity represent real disadvantages. However, the joint's strength evaluation represents a major challenge.

The geometry of the single lap joints tested was established according to the ASTM D1002-10 recommendations. Aluminium alloy 7075 T651 adherent and two type of adhesives (araldite AV 138M-1 with hardener HV 998, and araldite AW 106 with hardener HV 953U) were used. After the mechanical treatment of the surfaces, the adherents were cleaned in an acetone bath. The adhesives were cured at room temperature for 24 hours, under constant pressure applied through weights. The thickness of adhesives was carefully controlled at 0.3 mm, but no attempts were made to control the fillet geometry. The tests were carried out on a universal testing machine at 1.3 mm/min speed. Also, the mechanical properties in tensile and stress-strain curves for adherent and adhesives were obtained. A brittle behavior was observed for AV 138M-1 adhesive and a ductile one for AW106 adhesive.

A two-dimensional non-linear FEA was conducted using commercial ABAQUS package. The single lap bonded joints were meshed using 8 nodes CPE8 isoparametric elements and a converge study was performed considering 2, 4 and 6 finite elements through the adhesive thickness. A bi-linear behavior was considered for the aluminium adherent, while different material models (elastic, elasto-plastic and Neo Hooke hyperelastic) were considered for the adhesive. The numerical models were calibrated versus experimental load - displacement curve. Also the shear stress, maximum principal stress and equivalent stress were obtained from FEA.

Keywords: *single lap adhesive bonded joint, non-linear FEM.*

Acknowledgment

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project PN-II-ID-PCCA-2011-3.2-0068, contract number 206/2012.

Technical and technological means of core drilling in difficult conditions

Kudaikulova G.A.¹, Fedorov B.V.², Shintemirov A.K.³

kgulzhanabd@mail.ru

¹ LLP "Burmash", Almaty, Kazakhstan,

² Kazakh National Technical University – Department Geology and Oil-Gas
Business, 050013, Almaty, Kazakhstan

³ JSC "VolkovGeologya", Geology Prospecting Expedition–5", Almaty, Kazakhstan

In the article the combined technology of core drilling with application of specially developed technical and technological means is considered. Technical means are presented by new designs of the rock cutting tool (RCT) with application of Wireline system and the technology of drilling includes use of the newly developed formulas of drilling mud.

In work under the term of "difficult conditions" is meant as hard abrasive creviced rocks, and also the rocks inclined to inclined to caving and drilling mud loss. Such geological cuts rather often can be meet during the searching and investigation of fields in various regions of Kazakhstan. As an example, two geological cuts on two deposits: Kyzylshoky-Koktalsky and Mizek are given. The analysis of cuts shows that their top part is put rather soft, but inclined to caving, to sloughes and drilling mud loss by rocks. On the contrary, the lower part of cuts is presented by hard abrasive creviced rocks.

In a such mining-geological conditions a drilling company LLP «BURMASH» has applied a combined way of drilling. The top part of a cut was drilled in the traditional rotary core drilling with well washing with the special drilling muds developed for this purpose whereas the lower part of a cut had been drilled with the most advanced for today the rotary core drilling method and with application Wireline system.

As a RCT there had been used developed diamond bits with edge (sawtooth) profile of a diamond-bearing matrix which nominated as KSB-1 and KSB-2 indexes.

Comparative tests of bits of "Boart Longyear" company and developed bits were carried out on a gold field Kazakhstan deposit Mizek. Drilling was carried out on two types of rocks: andesyte porphyrite (X category of drilling capacity) and to intensively quartzizing tufas of andesyte compound (the XI category of drilling capacity). Wireline system technological mode parameters with a diameter of drilling of 76 mm were the following: rotational speed is– 640 – 710 rpm, axial loading – 1500 – 1600 DAN, a consumption of drilling mud – 40 – 50 l/min.

Had been made conclusions:

1. Use of the developed compositions of drilling muds allows to keep stability of walls of wells in difficult conditions and to ensure normal operating of RCT;
2. At drilling of hard abrasive rocks by means Wireline system diamond impregnated multilayered bits with a "sawtooth" equal-loaded profile of diamond-bearing layers of a matrix are the most effective.

Keywords: *drilling, drilling bit, rock cutting tool, Wireline system, drilling mud, diamond impregnated bit, difficult conditions of drilling, Kazakhstan deposits.*

Plasma Torch with Pyrolytic Graphite Electrode

Valeriy Lukyachshenko¹, Vladimir Messerle^{1,2}, Alexandr Ustimenko², Kuanysh Umbetkalyiev¹,
Victor Shevchenko¹
ust@physics.kz

¹Combustion Problems Institute, Almaty, Kazakhstan

²Research Institute of Experimental and Theoretical Physics, Almaty, Kazakhstan

There are plasma torches of linear circuits, containing coaxially mounted copper electrodes: a cylindrical cathode and an anode having an outlet nozzle in the form of a diffuser. The purpose of these plasma torches is to generate air plasma with outlet temperature from 3500 up to 5500 K, and use it for pulverized coal flame ignition and start up of pulverized coal fired boilers of thermal power plants. Life time of these plasma torches electrodes is critical and usually limited to 500 hours. Considered in this paper direct current arc plasma torch has the cathode life significantly exceeded 500 hours. To ensure the electrodes long life the process of hydrocarbon gas dissociation in the electric arc discharge is used. In accordance to this method atoms and ions of carbon from near-electrode plasma deposit on the active surface of the electrodes and form electrode carbon condensate which operates as “actual” electrode. To realize aforesaid the plasma torch has been developed and tested. Using special orifices propane/butane mixture is supplied to the zone of the arc conjunction to the copper water-cooled electrodes (cathode and anode). As a result inside the cathode cavity and internal surface of the anode medium of carbonic gas is formed. Linked with the arc in series, the magnetic coils guaranty stabilization of the discharge on the electrodes. The processes of propane/butane molecules dissociation and carbon atoms ionization start with the rise in temperature. Arisen from ionization positive carbon ions deposit onto the electrodes surface under the influence of near-cathode decline in potential and form coating of the electrode condensate regenerated continuously. This coating is “actual” cathode, deterioration of which is compensated by the flow of carbon ions and atoms. The coating thickness depends mainly on ratio of the flows propane/butane and air and the arc current and it does not exceed 500 μm . During experiments power of the plasma torch was varied from 76 to 132 kW and propane/butane flow in range of 0.4 – 0.7 l/m, thermal efficiency of the plasma torch reached 90%. At that mass averaged temperature on the exit of the plasma torch increased to 6000 K. The electrode condensate was examined using scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. It is found that the electrode condensate is composite carbonic stuff made of carbon nano-clusters which consist mainly of single and multi-wall carbon nanotubes and other carbonic forms including some quantity of the copper atoms intercalated to the carbonic matrix. As a result, a revolving pyrolytic graphite cathode layer prolongs life of the cathode several times.

Keywords: *plasma torch, hydrocarbon gas, pyrolytic graphite electrode, nanostructural carbon*

Research OF HIGH-Temperature Compression Property OF Ti₂AlN/TiAl Composites

Qing Wang
wqhit@hit.edu.cn

Harbin Institute of Technology
School of Materials Science and Engineering

The reactive hot-pressing technique was used to fabricate TiAl alloy and Ti₂AlN/TiAl composites with 20% volume fraction of Ti₂AlN particles. The behavior of high-temperature compressive deformation and high-temperature mechanical property of TiAl alloy and 20Ti₂AlN/TiAl composites under different temperatures and strain rates were studied. The feature of true stress-true strain curve and the relationship between high-temperature compressive strength and deformation parameters were analyzed. The mechanisms of hot compressive deformation and of strengthening of Ti₂AlN/TiAl composites were revealed through this study. The results showed that the compressive strengths of TiAl alloy and Ti₂AlN/TiAl composites with full lamellar microstructure decreased with temperature increasing, and increased with strain rates increasing; Compared with TiAl alloy, the increment of compressive strength of composites increased greatly at lower temperature and lower strain rates, and at higher temperature and higher strain rates; its maximum came up to 50% under the deformation conditions of 1100°C and 0.1s⁻¹. Based on the strength of TiAl alloy, a three-dimension state graph of the relationship between the strengthening effect, the deformation temperature and the strain rate of composites was established.

Plastic Deformation Flow Equations of Ti₂AlN/TiAl Composites

Dongli Sun
sundl1958@hit.edu.cn

Harbin Institute of Technology
Department of Materials Science

Compression tests of different temperatures and strain rates were carried out on TiAl alloy and Ti₂AlN particle reinforced TiAl matrix composites of two different volume fractions by Gleeble-1500D thermal simulated test machine. According to the experimental data, $\ln \dot{\epsilon}$ and $\ln \dot{\epsilon} - 1/T$ curves of different materials were obtained. The thermal deformation activation energy of three different materials in series of temperature and strain rate was calculated through the slope of each curve. Then plastic deformation flow equation was established. The study result showed that the thermal deformation stress of composite was higher than that of matrix alloy. The establishment of plastic deformation flow equation provided theoretical references for machine-shaping and application of Ti₂AlN/TiAl composites. Keywords: TiAl matrix composites, Ti₂AlN particles, plastic deformation flow equation

Explosive Surface Hardening of Austenitic Stainless Steel

Tunde Kovacs-Coskun
kovacs.tunde@bgk.uni-obuda.hu

Bánki Donát Faculty of Mechanical and Safety Engineering, Óbuda University,
Budapest 1034, Hungary

In this paper the effects of explosion hardening on the microstructure and the hardness of austenitic stainless steel have been studied. The optimum explosion hardening technology of austenitic stainless steel was researched. In case of the explosive hardening used direct and indirect hardening. The new technology is the indirect hardening setup. Austenitic stainless steels have high plasticity and can be easily cold formed. However, during cold processing the hardening phenomena always occurs. Upon the explosion impact, the deformation mechanism indicates a plastic deformation and this deformation induces martensite. The explosion hardening enhances the mechanical properties of the material, includes the wear resistance and hardness.

In case of indirect hardening as function of the setup parameters specifically the flayer plate position the hardening increased differently. It was find a relationship between the explosion hardening setup and the hardening level.

Keywords: *austenitic stainless steel, explosion hardening, microstructure, hardness, martensite*

SESSION 3

Advanced Nanomaterials with Pre-designed Properties

Effect of Si/Al molar ratio of hollow silica-alumina composite spheres on their activity for hydrolytic dehydrogenation of ammonia borane

Naoki Toyama¹, Tetsuo Umegaki¹, and Yoshiyuki Kojima¹
umegaki.tetsuo@nihon-u.ac.jp

¹ Department of Materials & Applied Chemistry, College of Science and Technology, Nihon university, 1-8-14, Kanda-Surugadai, Chiyoda-Ku, Tokyo 101-8308, Japan

Ammonia borane (NH₃BH₃) can release hydrogen in the presence of suitable solid acids or catalysts at room temperature. Among the solid acids, zeolites such as H-BEA and H-MOR show active for hydrolytic dehydrogenation of NH₃BH₃ [1]. For systematic investigation to reveal the effect of the morphology, we have focused on hollow spheres because of their intrinsic structural properties such as hollow spheres possess homogeneous shell structure. Hollow silica-alumina composite spheres were prepared by polystyrene (PS) template method, and PS templates were completely removed by calcination. The obtained hollow spheres show the same activity for hydrolytic dehydrogenation of NH₃BH₃ as these zeolites, and the activity depend on amount of acid sites of the hollow spheres [2]. On the other hands, it has been reported that amount of acid sites of samples depends on Si/Al molar ratio [3]. In this study, we investigate that influence of Si/Al molar ratio of hollow silica-alumina composite spheres on their morphology and activity for hydrolytic dehydrogenation of NH₃BH₃. From the transmission electron microscopy (TEM) images, homogeneous hollow spheres were obtained, and shell thickness of hollow spheres with Si/Al precursor molar ratio of 12.5, 25, 50, and 100 was about 5 nm. The activities of the hollow spheres with Si/Al precursor molar ratio of 12.5, 25, 50, and 100 for hydrolytic dehydrogenation of NH₃BH₃ were compared. The evolution of 7, 10, 10, and 5 mL hydrogen were finished in about 12, 13, 12, and 10 min in the presence of the hollow spheres with Si/Al precursor molar ratio of 12.5, 25, 50, and 100, respectively. The molar ratios of the hydrolytically generated hydrogen to the initial NH₃BH₃ in the presence of the hollow spheres with Si/Al precursor molar ratio of 12.5, 25, 50, and 100 were 2.0, 2.6, 2.6, and 1.7 (the theoretical value of 3.0), respectively. From the results, it is possible that the activity for hydrolytic dehydrogenation of NH₃BH₃ depends on surface properties of the hollow spheres.

Keywords: Ammonia borane, Si/Al molar ratio, Hollow silica-alumina composite spheres

References

- [1] M. Chandra, Q. Xu, J. Power Sources, 159, 855-860 (2006).
- [2] N. Toyama, T. Umegaki, Q. Xu, Y. Kojima, J. Jpn Inst. Energy, accepted(2014).
- [3] Y. T. Kim, K-D. Jung, E.D. Park, Appl. Catal., B 107, 177-187(2011).

The Particle Size Distribution Function in the Composite Films and Microwave Magnetic Properties

Leonid Kotov¹, Vladimir Ustyugov¹, Vladimir Vlasov¹, Viktor Turkov¹,
Yury Kalinin², Alexander Sitnikov², Evgeny Golubev³
kotovln@mail.ru

¹Department of Radio Physics and Electronics, Syktyvkar State University, 167001 Syktyvkar, Russia

²Department of Solid State Physics, Voronezh State Technical University, 394026 Voronezh, Russia

³Laboratory of Mineralogy, Institute of Geology Komi SC UB RAS, 167982 Syktyvkar, Russia

Composite films were obtained by the ion beam sputtering method in the argon atmospheres with compositions: $\{(Co_4-Fe_4-Zr_{0.7})_x+(Al_2O_3)_{1-x}\}$, $\{(Co_1-Nb_{0.2}-Ta_{0.05})_x+(SiO_2)_{1-x}\}$, $0.2 < x < 0.7$. Research is devoted to the definition of the size distribution function of metal granules in the composite films using atomic force microscope images. Size distributions of the metallic granules are studied for various concentrations of the metallic phase and annealing temperatures. It can be seen that increasing of the metal particles concentration decreases the amount of small size and amount of coarse particles increases. The annealing of the composite film results in a decrease of surface roughness of the film due to alloying of the metal fine granules and larger in the dielectric structure. The relative proportion of particles with a small effective size decreases. This process results in increase of large-sized particles that exceeds the maximum size of the particles observed in the films are not annealed. The dependence between structure of granules composite films and microwave magnetic properties is the aim of our study. Also theoretical model describing magnetic properties of composite structures based on micro magnetic is discussed. On the basis of the obtained data the microwave magnetic properties (FMR line width and resonance field) of composite films are calculated. The chosen model gives satisfactory results in the range of mean concentrations. The discrepancy between theory and experiment at low x of the metal is due to a limitation of the chosen model.

The work was done under financial support of RFBR (project 13-02-01401).

Studies of properties Al-P-O-zeolites with nano-crystalline structure

Sergei Kulkov¹, Alexander Buzimov¹, Wilhelm Eckl², Sandra Pappert²
buzimov92@gmail.com

¹ *ISPMS RAS / TSU, Tomsk, Russia*

² *Fraunhofer ICT, Pfinzthal, Germany*

It is well known that ceramic materials are the objects for intensive studies due to their unique properties. The possibility of synthesizing complex oxides such as "artificial zeolites" is promising for unique applications. Especially important is a consideration of zeolites during temperature changes and mechanical influence with the purpose to obtain of new species with the set physical and chemical properties. Wide application of zeolites caused the emergence of scientific research, aimed at the creation of new crystals with improved properties, non-toxic and environmentally safety.

It have been studied the structure, phase composition and properties of (Al-P-O)-based zeolites using x-ray analysis and BET-investigations for specific surface determinations after annealing at temperature up to 1000°C. It has been shown that there is no changing of crystal structure up to 1000°C, but amount of amorphous phase and specific surface are depended on temperature. This means that one can obtain the necessary specific surface by changing of annealing temperature which stipulate amount amorphous phase in system.

Modification of Titania Nanotubes by Ru-doping and Their Optical and Physico-chemical Properties

Hiroaki Sugiyama¹, Shun-Ichiro Tanaka¹, and Tohru Sekino²
sekino@tagen.tohoku.ac.jp

¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
Sendai 980-8577, Japan
Institute of Scientific and Industrials Research, Osaka University
Osaka 567-0047, Japan

Titania nanotube (TiO₂ nanotubes, TNT) is a unique low-dimensional nanostructured material that consists from nanosized tubular of TiO₂. Because of its excellent physical-chemical functions, the TNTs have attracted great attention from the view point of future applications in environmental cleaning, energy conversion/harvesting, sensors, biocompatible materials fields. Further, TNT has unique multifunctionality that is a synergy of molecular adsorption and photocatalytic properties, which does not exist in common TiO₂ nanoparticles. We have thus focused on further tuning of TNTs' structures, physical, chemical, optical and photochemical properties by doping metal ions such as Cr, V, Nb, Sn etc. In this research, we have selected ruthenium (Ru) as the dopant to TNTs, and aimed to investigate the doping effect of Ru on TNTs fundamental properties and functions for developing environmental friendly and/or energy-related materials. Because Ru is a transition metal belonging to the platinum group, it is widely used in catalysts and organometallic compounds such as dye molecules for sensitized solar cells, which implies us that the Ru doping might enhance the photochemical and /or physico-chemical functions of TNTs.

Ru-doped TNTs were successfully obtained by the low-temperature solution chemical synthesis route: TiO₂ raw powder and RuCl₃ (Ru; ~10 mol%) was refluxed for 24h at 110°C in 10 M NaOH solution. The product was washed by distilled water many times and neutralized by 0.1 M HCl.

Nanotubular titania with the diameter of below 15nm was confirmed by electron microscopies. X-ray diffraction analysis revealed that the products had weak crystallinity, which was the typical for as-synthesized TNTs. UV-visible light diffused reflectance spectroscopy revealed that reflectance at visible light region decreased with the increase in Ru content. Optical bandgap energy was found to be 2.08 eV for 10mol%Ru-TNT. Thus it is expected that Ru-doped TNT might exhibit visible-light responsibility in photocatalytic and/or photo-chemical functions. Detailed relationships between structures and physical, optical, and photochemical properties of Ru-TNT will be discussed.

Keywords: *titania nanotube, ruthenium, doping, chemical processing, nanostructure, optical properties, visible light responsibility*

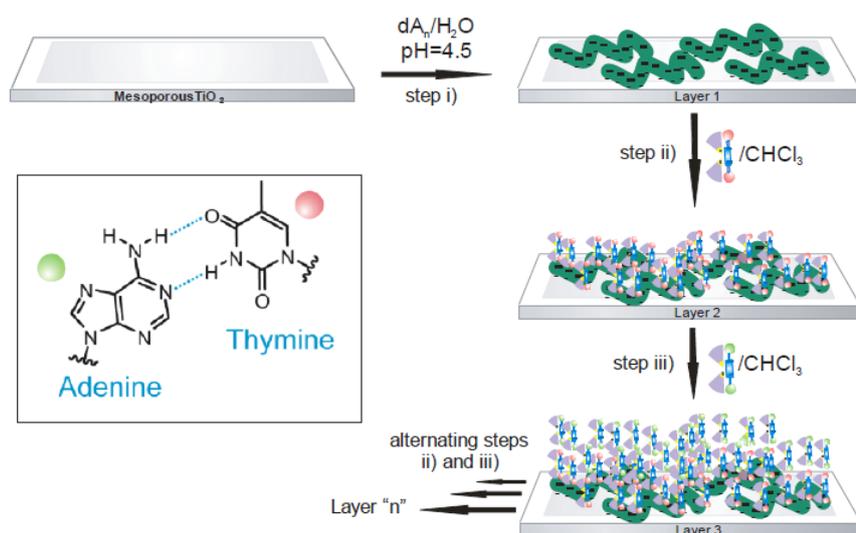
Hydrogen-bonded layer-by-layer modification of mesoporous TiO₂ films for electrochromic devices

Marius Ciobanu, Simona Asaftei
maciobanu@uos.de, sasaftei@uos.de

Department of Organic Materials Chemistry, Institute of Chemistry of New Materials
University of Osnabrück, 49069 Osnabrück, Germany

The layer by layer (LBL) technique [1] has become a versatile option for making nanostructured films under mild conditions, which is particularly important for preserving activity of biomolecules. The advantage of this coating method are the different possibilities to deposit the molecule on the solid surface using alternated dipping of the substrate to be coated in solutions containing the interacting species by electrostatic or hydrophobic interactions, covalent or hydrogen bond donors acceptors [2]. In this work we modified the surface of mesoporous TiO₂ thin films with electroactive viologen-nucleobase derivatives using complementary hydrogen bonding between adenine and thymine nucleobases. The underlying principle is based on repetitive and donor-acceptor forming hydrogen bonds between thymine and adenine units on a monolayer of an oligonucleotide (dAn) modified TiO₂ electrode. Cyclic voltammetry and spectroelectrochemical methods (SEC-UV-VIS) have been employed for the characterization of the modified films. The stability of the deposited hydrophobic layers was checked by desorption experiments in water. The modified TiO₂ mesoporous film with viologen-nucleobase derivatives can be successfully incorporate as electrochromic component in construction of type-III electrochromic displays. [3]

Keywords: layer-by-layer, electrochromism, adenine, thymine, viologen, oligonucleotide, TiO₂



References

- [1]. R. M. Iost et al., *Biosensors and Bioelectronics*, 2012, 31, 1-10.
- [2]. U. Manna et al., *Biomacromolecules*, 2009, 10, 2632-2639.
- [3]. P. M. S. Monk et al., *Electrochromism and Electrochromic Devices*, Cambridge University Press, New York, 2007.

Laser-induced crystallization process in lead-fluorine glassceramics doped with neodymium

Anastasiya Bibik, Rustam Nuryev, Vladimir Aseev, Elena Kolobkova, Nikolay Nikonorov
anastasiya.bibik@list.ru

University ITMO, 199034 Saint-Petersburg, Russia

Since recently the transparent fluorine-containing glassceramics matrices, containing the neodymium ions, included into the fluorite-like nanocrystalline phases, are drawing the attention to the series of spectroscopy advantages. It is obvious that from the point of view of laser active media development optimal are the materials, which are characterized by the low-frequency phonon spectrum and by the low content of the OH-groups, because in this case one can reduce the excitation energy losses due to the multi-phonon quenching process. Thus, transparent fluorine-containing nano-glassceramics doped with rare earth ions are promising media for fiber laser, solar cell up- and downconvertors, phosphors for white LED and broadband optical amplifiers.

We have synthesized the glasses of the system (mol%) $30\text{SiO}_2\text{-}15\text{AlO}_{3/2}\text{-}18\text{PbF}_2\text{-}29\text{CdF}_2\text{-}5\text{ZnF}_2\text{-}x\text{NdF}_3\text{-}(3-x)\text{YF}_3$, where x was varied for 0 up to 3.0. It was shown that neodymium ions play a role of nucleation centers for PbOYF_3 crystal phase growth. The size of crystalline phase achieves 40 nm. The dependence of the low-level cell size and the volume of crystal fraction on heat-treatment conditions were determined. Spectral and luminescence properties of nano-glassceramics have been investigated in visible and IR ranges. It was shown that emitting probabilities of different transitions changed during the thermal treatment. The entry of rare-earth ions in crystal phase results in broadening of emission spectra because of fluoride surrounding. For example, for Er-doped nano-glassceramics the band width of emission spectrum at 1.55 μm achieves 70 nm. RE-doped nano-glassceramics are promising candidates for different photonics applications, like fiber and waveguide lasers and sensors.

It was shown that the laser-induced heating of oxyfluoride glass results in precipitation of crystalline phase $\text{PbY}(1-x)\text{Nd}(x)\text{OF}_3$. This method allows us to control the size of nanoparticles. Moreover it was shown that the laser treatment can completely damage the crystalline phase.

Keywords: X-ray Diffraction, nano-glassceramics, neodymium, crystallization

Band gap engineering of ZnO via chemical decoration of its nanoparticles with transition metal oxides

Elena Trusova¹, Kirill Vokhmintcev¹, Alexey Kirichenko^{1,2}
Trusova03@gmail.com

¹A.A. Baikov Institute of Metallurgy and Material Science of RAS, Moscow, Russia

²Technological Institute of Superhard and Novel Carbon Materials, Moscow, Russia

Nanostructured ZnO is promising raw product for photovoltaics and photocatalysis. As known many physical-chemical properties of crystalline materials depend on the band gap value and structure. So, it's important that the band gap can be controlled precisely. We present a chemical decoration of ZnO nanoparticles as the method of its band gap engineering. Previously, we reported on decoration of ZnO nanoparticles with Bi and Ni oxides, and presented evidence of its chemical character [J. Am. Ceram. Soc. 97 [1] 135-140 (2014)]. In this report we enlarge the number of decorating metal oxides and show the possibilities of chemical decorating for band gap engineering. One or two oxides from the following metal series Bi, Ce, Cr, Cu, Ni, Y, Zr were deposited on the ZnO surface by using of modified sol-gel synthesis. Initial nanoparticles of ZnO have sizes 30-40 nm. The characterization of obtained compositions was carried out using XRD, TEM, Raman, FT-IR, UV-vis.-spectroscopy, BET. It has been shown that the initial ZnO had a mesoporous structure which was kept after decorating, however, the mesopore size, volume and surface area decreased. FTIR data show the chemical interaction between ZnO surface and structural elements of deposited oxides, which was confirmed by new vibrational levels observed in Raman spectra. We have assumed that shifts of the characteristic bands in the Raman spectra of composites were caused the formation of 2D interface between ZnO surface and nanoparticles of decorating metal oxides. UV Spectroscopy data were used to calculate the band gap by the J. Tauc plot method, and some regularities were found. It was shown that chemical decoration of ZnO nanoparticles with different metal oxides can both decrease and increase band gap, as well as leads to form its fine structure.

The work was supported by the RFBR, grants №№ 13-03-00350_a and 14-02-00517_a.

Redox synthesis of metal/carbon nanocomposites

Vladimir Kodolov^{1,2,3}, Vera Trineeva^{1,3,4},
kodol@istu.ru

¹Basic Research – High Educational Centre of Chemical Physics & Mesoscopy, Udmurt Scientific Centre, Ural Division, Russian Academy of Sciences, Izhevsk, Udmurt Republic, Russia

²M.T. Kalashnikov Izhevsk State Technical University, Izhevsk, Udmurt Republic, Russia

³Research Innovation Centre at Izhevsk Electromechanical Plant “KUPOL”,
Izhevsk, Udmurt Republic, Russia

⁴Institute of Mechanics, Ural Division, Russian Academy of Sciences,
Izhevsk, Udmurt Republic, Russia

The synthesis of nanostructures in nanoreactors of polymeric matrixes is represented the perspective trend for nanochemistry development. Nanoreactors can be compared with specific nanostructures representing limited space regions in which chemical particles orientate creating “transition state” prior to the formation of the desired nanoparticle. Nanoreactors have a definite activity which predetermines the creation of the corresponding product. When nanosized particles are formed in nanoreactors, their shape and dimensions can be the reflection of shape and dimensions of the nanoreactor. The investigation of redox synthesis of Metal/Carbon nanocomposites in nanoreactors of polymeric matrixes is realized in three stages: 1) The computational designing of nanoreactors filled by metal containing phase and quantum chemical modeling of processes within nanoreactors. 2) The experimental designing and nanoreactors filling by metal containing phase with using two methods (the mixing of salt solution with the solution of functional polymer, for example, polyvinyl alcohol; or the common degeneration of polymeric phase with metal containing phase). 3) The properly redox synthesis of metal/carbon nanocomposites in nanoreactors of polymeric matrixes at narrow temperature intervals.

The method of metal/carbon nanocomposite synthesis applied has the following advantages: 1) The perspectives of this investigation are looked through in an opportunity of thin regulation of processes and the entering of corrective amendments during processes. 2) Wide application of independent modern experimental and theoretical analysis methods to control the technological process. 3) Technology developed allows synthesizing a wide range of metal/carbon nanocomposites depending on the process conditions. 4) Process does not require the use of inert or reduction atmospheres and specially prepared catalysts. 5) Method of obtaining metal/carbon nanocomposites allows applying secondary raw materials. In this investigation the possibilities of developing new ideas about self-organization processes during redox synthesis within nanoreactors of polymeric matrixes as well as about nanostructures and nanosystems are discussed on the example of metal/carbon nanocomposites. It is proposed to consider the obtaining of metal/carbon nanocomposites in nanoreactors of polymeric matrixes as self-organization process similar to the formation of ordered phases. The perspectives of this investigation are looked through in an opportunity of thin regulation of processes and the entering of corrective amendments during processes

Energetic characteristics of metal/carbon nanocomposites

Vladimir Kodolov^{1,2,3}, Vera Trineeva^{1,3,4}, Yuri Vasil'chenko^{1,2,3}
kodol@istu.ru

¹Basic Research – High Educational Centre of Chemical Physics & Mesoscopy, Udmurt Scientific Centre, Ural Division, Russian Academy of Sciences, Izhevsk, Udmurt Republic, Russia

²M.T. Kalashnikov Izhevsk State Technical University, Izhevsk, Udmurt Republic, Russia

³Research Innovation Centre at Izhevsk Electromechanical Plant “KUPOL”
Izhevsk, Udmurt Republic, Russia

⁴Institute of Mechanics, Ural Division, Russian Academy of Sciences
Izhevsk, Udmurt Republic, Russia

The metal/carbon nanocomposites are considered as super molecules. Therefore their surface energies analogously energy of usual molecules consists portions of energy which correspond to progressive, rotation and vibration motions and also electronic motion. From the metal/carbon nanocomposites Raman and IR spectra analysis it follows that the skeleton vibration of them on the vibrations frequencies corresponds to ultrasonic vibrations. The nanocomposite vibrations energy values are determined by the corresponding nanoparticles sizes and masses. Usually metal/carbon nanocomposites have the great dipole moment. Therefore it is possible the proposition that nanocomposite is vibrator which radiates electromagnetic waves. The nanocomposite vibration emission in medium is determined by their dielectric characteristics and the corresponding functional groups presence in medium. At the metal/carbon nanocomposites obtaining the interaction of polymeric matrix with metal containing phase leads to formation of metal clusters covered by carbon shells accompanied by metal electron structure changes. In some cases the medium characteristics influence on nanocomposites throw into the increasing of nanocomposite surface energy portion, which concerns with changes of their electron structure and equally with electron structure of medium. In these cases the growth of metal atomic magnetic moment is observed that corresponds to the unpaired electron number increasing. The considerable changes of metal atomic magnetic moments in nanocomposites proceed when the phosphorus atoms include to carbon shells of nanocomposites. Thus, according to the analysis of metal/carbon nanocomposites characteristics, which are determined by their sizes and content, their activities are stipulated the correspondent dipole moments and vibration energies. The electromagnetic waves are formed at the ultrasonic vibration of metal/carbon nanocomposites. These waves stimulate the changes of electron structure and the growth of magnetic moments of clusters within nanocomposites. It is shown that the nanocomposites vibration energies depend on their average masses. However the specific surface of metal/carbon nanocomposites particles changes in dependence on the nature of nanocomposite in other order than the correspondent order of the vibration energies.

Therefore the energetic characteristics of metal/carbon nanocomposites are more important for the activity determination in comparison with their size characteristics.

Modification of polymeric materials by super small quantities of metal/carbon nanocomposites

Vladimir Kodolov^{1,2,3}, Vera Trineeva^{1,3,4}, Yan Polyotov^{1,2}, Yuri Pershin^{1,2}
kodol@istu.ru

¹Basic Research – High Educational Centre of Chemical Physics & Mesoscopy, Udmurt Scientific Centre, Ural Division, Russian Academy of Sciences, Izhevsk, Udmurt Republic, Russia

²M.T. Kalashnikov Izhevsk State Technical University, Izhevsk, Udmurt Republic, Russia

³Research Innovation Centre at Izhevsk Electromechanical Plant “KUPOL”
Izhevsk, Udmurt Republic, Russia

⁴Institute of Mechanics, Ural Division, Russian Academy of Sciences
Izhevsk, Udmurt Republic, Russia

The essential changes of polymeric materials structures and properties at the metal/carbon nanocomposites addition in them are experimentally shown in papers. The hypothesis of corresponding nanostructures super small quantities influence on media through nanostructures vibrations transfer on media molecules when these vibrations near to ultrasound vibrations is proposed. Further this hypothesis is confirmed in some measure by the media IR spectra intensities increasing at the addition of metal/carbon nanocomposites in these media. In this case the self-organization of media molecules and the changes of corresponding media properties are found. In liquid media the self-organization effect depend on media viscosity and its polarity. At the same time the intensity increasing in IR spectra of some media as well as the C1s lines widening in x ray photoelectron spectra is discovered. This fact can be explained by the media electronic structure changes, and also by the coordination interaction of nanocomposites with media molecules. The observed experimental results demand an answer with point of view concerning fundamentals of polymeric materials modification by super small quantities of metal/carbon nanocomposites. The metal/carbon nanocomposite vibration energy transference through electromagnetic waves on the medium molecules is confirmed by the increasing of intensity in IR spectra for the fine dispersed suspensions which contain the super small quantities of metal/carbon nanocomposite. The stability of correspondent suspensions changes in dependence on the medium nature. The essential changes of lines intensity in IR spectra take place for the polar liquids. The facts observed are correlated with growth of nanocomposites activities in the self organization processes at the materials production. The action of electromagnetic radiation of nanocomposite super molecule on polymeric polar compositions will be lead to the IR radiation increasing of correspondent media as well as to change of their electron state. It is noted that the surface energy vibration portion of nanocomposite super molecule is only realized at its super small quantities addition in the correspondent polymeric systems. Besides the growth of lines intensity in IR spectra takes place. When there is the increasing of the nanocomposite content in the polymeric systems, the growth of the rotation and electron portion of surface energy is observed. In this case the electromagnetic radiation part is decreased and the electromagnetic waves transference velocity is decreased too.

SESSION 4

Biomaterials Derived Ceramics and Composites

Using Coca-Cola® as odd synthesis parent medium for calcium phosphate precipitation

Mauro Mazzocchi, Giancarlo Celotti
mauro.mazzocchi@istec.cnr.it

Institute for Science and Technology of Ceramics- National Council of Research, Faenza, Italy

Reading the ingredient list of the Coca-Cola®, (The Coca-Cola® Co., Atlanta, USA), it is impossible not to notice that beside sugars, CO₂, and undisclosed additives, the orthophosphoric acid, H₃PO₄, is present (as food additive: E338 in EU notification).

Considering the ascertained power of dissolution of the acidic content of the beverage acting on teeth enamel, as well as the consequences for huge phosphate assumptions inhibiting bone mineralization, was idealised the precipitation of a Ca-phosphate from Coca-Cola as reverse concept and thus pursued in a mere feasibility study by using it directly and its known content in orthophosphoric acid.

Hydroxyapatite composition is close to that of the mineral fraction of bone and teeth and since 40 years ago it has been the most used alloplastic material to replace bone tissue in skeletal surgery: starting from its stoichiometric formula it has been synthesized until nowadays with a number of crossed ionic substitutions to improve and render it much more biomimetic and biosoluble.

A stoichiometric HA may be obtained through pure reagents in different synthesis routes (acid-base precipitation in aqueous environment, mechanochemical, hydrothermal, sol-gel, etc.).

In this work, using one Coca-Cola® bottle (1.5 lt), a simple route for acid-base precipitation at low temperature was carried out to yield low crystallinity HA. XRD analyses and SEM-EDS characterization of the precipitate before and after a mild calcination, to burn out organics, were carried out confirming the successful synthesis and the structural-physical characteristics of the obtained phosphate, notwithstanding the presence of carbohydrate macromolecules in the parent solution.

The significant presence of hydrocarbonic acid, as dissolved CO₂ was also taken into account of eventual assessable structural substitutions (in A or B site) within the phosphate molecule, if any.

Keywords: *Ca-phosphate, hydroxyapatite, wet synthesis, acid-base precipitation*

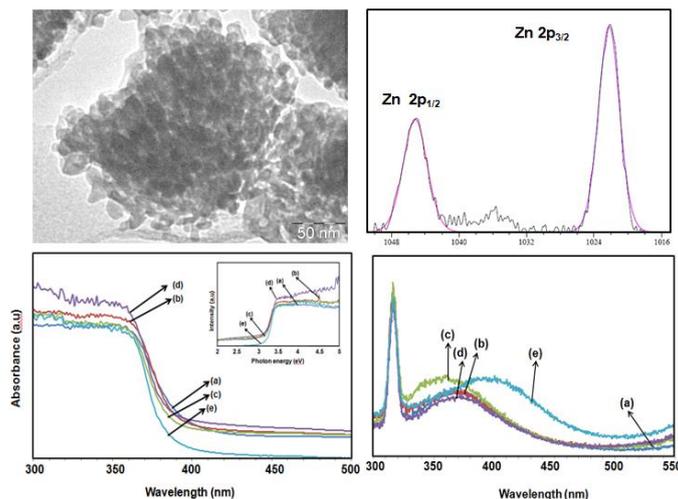
Size controlled morphological study using natural Gums: A Green approach

B. Sreedhar¹, M.Sulochana², D. Keerthi Devi¹, Ch. Satya Vani³, N.Venkatasubba Naidu^{2,*}
sreedharb@iict.res.in, mungasulochana@gmail.com

¹Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology (Council of Scientific and Industrial Research), Hyderabad, Andhra Pradesh, 500607, India

²Department of Chemistry, Sri Venkateswara University, Tirupati, Andhra Pradesh, 517 502, India.

³Department of Chemistry, SR International Institute of Technology, Rampally, Keesara (M), RR District, Andhra Pradesh, 501301, India.



Zinc oxide is an industrial important material due to its wide applications in luminescence, solar cells, light emitting diodes, optical devices, antibacterial agents and as photo catalysts. Tuning the reaction conditions such as concentration, time variation and temperature lead to the formation of nanoparticles with different morphological growth, size and properties. Gums - natural polysaccharides - consist of a β -(1-3)-galactose backbone with linked branches of arabinose and rhamnose, which terminate in glucuronic acid. In the present work, various morphologies of zinc oxide nanoparticles such as globular structures with a size range of 10-23 nm were identified. The experimental results revealed that gums act as a structure directing agent of ZnO deposition and it is essential to obtain ZnO nanoparticles in low temperature precipitation experiments. The observations showed that screw capped method are more effective than oil bath method in controlling the size of nanoparticles. The particles were well characterized by TEM, XRD, FT-IR, TGA, UV-DRS, XPS, PL-spectrum, Raman and the antimicrobial activity was studied using four different pathogenic bacteria. To explore the growth possible mechanism, different concentrations of various gums with varied mole/reactant concentration were studied.

Keywords: Zinc Oxide, Natural Gums, Nanoparticles, Screw capped, PL spectrum, Antibacterial.

Bioceramic Scaffolds Manufacturing by Laser 3D Printing

Fwu-Hsing Liu
fhliu@mail.lhu.edu.tw

Lunghwa University of Sci. and Tech. Taoyuan, Taiwan

In this work, a hydroxyapatite (HA) bioceramic and a silica binder were used as the raw materials for manufacturing bioceramic bone scaffold after sintering by a laser beam in a home-made 3d printing (3DP) machine. A controlled pore size of porous bone scaffold can be fabricated after the ceramic slurry, mixed by HA and silica, is sintered under suitable laser processing parameters. Results indicate that the bending strength and compressive strength of the scaffold can be improved after heat-treatment at 1200°C; for 2 hour. While simultaneously increasing surface roughness conducive to osteoprogenitor cell adhesion. MTT method and SEM observations confirmed that bone scaffolds fabricated under the optimal manufacturing process possess suitable biocompatibility and mechanical properties, allowing smooth adhesion and proliferation of osteoblast-like cells. Therefore, this process has great potential for development in the field of tissue engineering (TE).

Antimicrobial Activity of TiO₂ Nanoparticles and Nanocomposite Implants on Microorganisms Causing Dental Plaques

Anitha Thomas M. Shailaja Raj
anitha.thomas@sfc.ac.in

¹ Department of Microbiology, St Francis College for Women, Begumpet, Hyderabad.

In recent years, Nanotechnology has been flourishing. Nano-structured materials are attracting a great deal of attention because of their potential for achieving specific processes and selectivity, especially in biological and pharmaceutical applications. The present study deals with isolation and characterization of organisms causing dental plaques. Forty isolates were collected from patients at Savitha dental clinic, Kukatpally. These isolates indicated the presence of bacteria as well as fungi. The isolates were characterised by cultural and biochemical methods according to Bergeys manual of Systematic Bacteriology. The antimicrobial activity of titanium dioxide nanoparticles were checked against all these organisms responsible for plaque formation and among these 40 dental isolates titanium dioxide nanoparticles showed good inhibition against 18 isolates. The antimicrobial activity of Isopropanol as control, Titanium dioxide, and titanium dioxide nanoparticle were comparatively analysed and results proved that TiO₂ nanoparticles showed higher activity compared to the other two. The minimum inhibitory concentration of TiO₂ nanoparticles were carried out. TiO₂ nanoparticles were also incorporated into certain mouthwashes to check the activity and stability of these nanoparticles. The results obtained reveals the fact that TiO₂ nanoparticles when used in combination with chlorhexidine, the inhibition of the organisms is slightly more compared to chlorhexidine alone thus having enhanced activity. But when the combination of TiO₂ was used with Colgate Plax and Listerine the synergistic effect of TiO₂ and the mouthwashes was low in inhibiting the growth of the bacteria. From the above studies we can conclude that TiO₂ nanoparticles can be used for controlling organisms causing dental plaques and TiO₂ nanoparticles can also be used with some mouthwashes like chlorhexidine for enhanced antimicrobial activity. X-Ray Diffraction studies were used to analyze particles size and it was found to be 26 nm. Further studies will be carried out to control the oral biofilm formation by preparing TiO₂ nanocomposites alone or in combinations with other nanoparticles and TiO₂ implants as novel nanoparticles. Coating dental implants with nanocomposites containing titanium dioxide nanoparticles holds promise for improving the longevity of the implants. The nanoparticles could also offer antimicrobial properties and improve healing following implant surgery.

Key words: *Nanocomposites, antimicrobial activity, implant surgery*

Influence of Hemp Fibers Pre-processing on Low Density Polyethylene Matrix Composites Properties

Silvija Kukle¹, Zane Zelča² and Janis Kajaks³
skukle@latnet.lv

^{1,2} Institute of Textile Technologies and Design, Riga Technical University, Latvia
³ Department of Polymer Material Technologies, Riga Technical University, Latvia

Linear low density polyethylene (LLDPE) excellent environmental stress crack resistance, chemical inertness, low temperature impact, strength and resistance to ultraviolet exposure, rigidity, toughness combined with a low density, good moldability and reasonable price have attracted attention as potential matrix for natural fibers reinforced composites.

Hemp plants as cost effective, renewable, high productive, low density and CO₂ neutral, biodegradable resource are investigated intensively for a range of applications. As our previous investigations show without hemp fibres pre-processing the best mechanical properties were achieved with 30 %wt fibres reinforcement, with water sorption capability after 240 h in a range from 7.1 to 8.8 %wt. In present research with hemp fibres (cutted in length up to 1 mm) reinforced LLDPE (grade LL 6201) matrix composites with hemp fibres content in a range from 30 to 45 wt.% with four different pre-processing technologies were produced and such their properties as tensile strength and elongation at break, tensile modulus, melt flow index, microhardness and water absorption dynamics were investigated.. For evaluation of fluidity capillary viscosimetry was used and melt flow index (MFI) evaluated for all variants. MFI meaaurements for composites with hemp fibres content 30 %wt depending on pre-processing technology applied gives values in a range from 0.75 g/10min. to 16.76 g/10min. which are sufficient to process these composites with traditional polymer processing methods (extrusion, compression moulding). In distinction from our previous studies, MFI of two present variants with fibers pre-processing were high enough to increase hemp fiber content from 30 to 45-50 %wt without increase of water sorption capability.

Keywords: *Linear low density polyethylene, matrix, hemp fibers, composite, properties*

Investigation of the electric field for the prediction of earthquakes

Metin SALTIK, Ertan YANIKOĞLU
saltik@sakarya.edu.tr

Sakarya University
SMYO-Adapazari, Electronic-Engineering, Esentepe-Serdivan

The present paper reveals that the air contains electromagnetic energy of extremely low frequency, low amplitude as well as of a low phase speed. The energy is of great interest because of its impact on certain biological processes. It is created by the interaction of two well known phenomena. The rotation of the earth generates 24-hour periods currents in the magnetosphere, known as the Birkeland currents. The currents generate transverse electromagnetic waves (EM waves) propagating parallel to the geomagnetic field lines. Furthermore, the air and the earth crust contain electrons caused by the global electric circuit. The electric field vectors of the EM waves exert a force on these electrons, causing them to oscillate and thus generate currents of extremely low frequency both in the air and in the earth crust. A theoretical model of the system is presented and measurement techniques are described.

Keywords: *ELF; ELF EM waves; Atmospheric electricity; resonance in the air*

Effect of Fiber Orientation on The Mechanical Properties of Continuous Date Palm Leaf - Glass Hybrid Fiber Reinforced Epoxy Composites

Daniel Roberto Hernández Ochoa, Elsadig Mahdi Ahmed Saad
drhochoa@qu.edu.qa

Mechanical and Industrial Engineering Department, College of Engineering, Qatar University, P.O.
Box 2713, Doha, Qatar

This paper examines the effect of fiber orientation (0° , 15° , 30° , 45° , 60° , 75° and 90°) on the tensile behavior of continuous date palm leaf fiber (DPLF) – Glass (GF) hybrid reinforced epoxy composites. Laminate with 33% volume fraction of reinforcement (12% DPLF and 21% GF) was prepared using hand layout manufacturing technique. The fiber morphology, fracture surfaces and sections through the coupon were examined by means of scanning electron microscopy (SEM). The mechanical properties such as maximum stress, Young's modulus, energy absorption, percentage total elongation at fracture were computed and the tensile stress/displacement curves were plotted. The results showed that laminate with 45° DPLF orientation decreased the maximum stress 23.5%, 57.8% total elongation at fracture and increased the Young's modulus 43.6%. SEM composite morphology study indicates that epoxy uptake area reached up to 31% of DPLF cross section area and showed that delamination, fiber breakage and fiber pull out were the major features of reinforced composites damage characteristics.

Keywords: *Date palm fiber; Epoxy; Tensile; Energy absorption; Hybrid, Biocomposite*

Polymer nanocomposite - A novel antimicrobial agent in treating Diabetic foot ulcers

M. Shailaja Raj
shailarm@yahoo.com

St. Francis College for Women, Begumpet, Hyderabad, India

Diabetic foot ulcer is a major complication of diabetes mellitus. It occurs in 15% of all diabetic patients and precedes 84% of all lower leg amputations. This may occur due to macro and micro vascular complications, including failure of the wound healing process. Diabetes mellitus is a metabolic disorder that impedes the wound healing process. Many histopathological studies show a prolonged inflammatory phase in diabetic wounds, which causes a delay in the formation of mature granulation tissue and a parallel reduction in wound tensile strength.

The most common risk factors for ulcer formation include diabetic neuropathy, structural foot deformity and peripheral arterial occlusive disease. Treatment consists of appropriate bandages, antibiotics, debridement, arterial revascularization and plate-rich fibrin therapies. Recently, the mortality rate is increasing due to foot ulcer complications and healed ulcers often recur. The pathogenesis of foot ulceration is complex, clinical presentation variable and management requires early expert assessment. Despite treatment, ulcers readily become chronic wounds. Diabetic foot ulcers have been neglected in health-care research and planning. Furthermore, the pathological processes are poorly understood and poorly taught. Thus, there is a tremendous need to do research on diabetic foot ulcers and in identifying organisms responsible for causing such ulcers.

The present study concentrates on the isolation and identification of the microorganisms that are responsible for causing foot ulcers in diabetic patients. About six strains were isolated directly from the infected foot ulcer and were identified based on Bergy's manual as *Serratia fonticola*, *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Streptococcus* and *Bacillus sphaericus*. These strains were further subjected to antibiotic susceptibility test and polymer sensitivity test. The polymer liquid resin complexed with polyvinyl alcohol gave us hope that it could be used as an effective antimicrobial against these organisms. Further study is envisaged to be carried out with polymer nanocomposite which could be used as new generation antimicrobial agent.

Films and coatings of nanocrystalline silver-polyvinyl alcohol (PVA)-melamine formaldehyde resin (MFR) composites in cost effective application for wound dressings in diabetic foot disease.

Rita Kakkar¹, Kalpana Madgula¹, Y.V.Saritha Nehru¹, Jayesh Kakkar²
Kakkarrita53@gmail.com

¹ Department of Chemistry St.Francis College for Women, Begumpet, Hyderabad

²Consultant Diabetic and Wound Care Surgeon, Vivekananda Hospital, , Begumpet, Hyderabad

Globally there is a large population of people suffering with diabetes. A large percentage of these patients develop foot ulcers at some point which heal very slowly and can worsen very rapidly. The use of silver nanoparticles in silver release dressings and in management of infected wounds is important, as several pathogenic bacteria have developed resistance against various antibiotics. Such dressings vary in technological nature of their silver content ,and release .Use of silver dressings in recent times have a considerable challenge of lacking cost effectiveness.

Prepared PVA-MFR composite films and coatings have been found to have good level of antimicrobial activity. Colloidal Nanocrystalline silver was prepared characterised and tested for its antimicrobial activity. Nanosilver was then impregnated into the PVA-MFR composite and nano-composite casted into films, soaked into polyvinyl foam, and also coated on whattmann paper. Antimicrobial efficacy of such prepared dressing materials tested .

Tissues from the wound depth of six diabetic foot diseased patients were collected to isolate and identify the microorganisms responsible for causing foot ulcers in diabetic patients and study polymer sensitivity . PVA-MFR dressings are found to be antimicrobial against S Aureus, P.Vulgaris, PSeudomonas and Enlebater species in these samples. In each case antimicrobial activity is enhanced in NANO SILVER impregnated PVA-MFR dressing materials.

These dressings can be cost effective for the reason that efficacy of nano silver is superimposed on antimicrobial activity of cheaper PVA-MFR composite. The material can be easily cast into thin films of desired thickness , size .

Keywords: *Wound dressings , Nano silver composite, Antimicrobial , diabetic ulcers ,PVA-MFR*

SESSION 5

Glasses, Coatings and Related Materials

Research Progress on Microwave Plasma Chemical Vapor Deposited Graphene

Hao Wang¹, Weidong Man²
haowangboiling@gmail.com

¹ Central Europe University, Business

² Wuhan Institute of Technology, Plasma Chemistry and Advanced Materials

Microwave plasma chemical vapor deposition (MPCVD) is a newly developed method for preparation of graphene in recent years. It has obvious advantages on low-temperature processing, accessibility to economical scale and a range of substrate materials, as well as selective doping approaches; compared to traditional thermal chemical vapor deposition (T-CVD), MPCVD is gradually becoming attractive for industrial graphene manufacturers [1]. This article is a review of recent research progress of MPCVD in terms of graphene growth and processing. Some conventional methods are referenced in comparison with the MPCVD results; recent experiments are updated mainly in light of micro-Raman and optical transmittance spectra. At the end, perspective applications and development trends of MPCVD are dictated.

[1] K.S.Novoselov, L.Colombo, P.R.Gellert, et al, Nature 2012 (490) 192.

Thermally induced indentation recovery in terbium doped aluminophosphate glasses

Bogdan Alexandru Sava ¹, Olga Shikimaka ², Daria Grabco ³, Mihail Elisa, Lucica Boroica ²
E. Harea², C. Pyrtsac²
savabogdanalexandru@yahoo.com

¹ Department of Lasers, National Institute for Lasers, Plasma and Radiation Physics, Magurele, Romania

² Laboratory of Mechanical Properties of Materials, Institute of Applied Physics of the Academy of Sciences of Moldova, MD-2028 Chisinau, Moldova

³ Department of Optospintronics, National Institute for R&D in Optoelectronics INOE2000, Magurele, Romania

The mechanical behavior of terbium doped aluminophosphate glasses ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{BaO}-\text{La}_2\text{O}_3-\text{P}_2\text{O}_5-\text{Tb}_2\text{O}_3$) was investigated using the nanoindentation technique and atomic force microscopy (AFM). The glass was obtained through a wet chemical raw materials processing technique with subsequent melting and annealing that ensured a good homogeneity and low defect structure of glasses. As a result the mechanical parameters like hardness (H) and Young's modulus (E) demonstrated rather high values. It was found that H and E depend on the load applied (20-900 mN) and the loading-unloading rate (0,5-90 mN/s) and obtain their maximum values for lower loads and higher deformation rates and range from 7,6 to 4,4 GPa for H and from 73,3 to 52,3 GPa for E. Upon heating the indented sample up to 400°C, below the glass transition temperature, the partial depth recovery of indentations was revealed (see Figure). The recovery ratio was found to depend as well on the indentation load and loading-unloading rate. The maximum recovery (44%) exhibited the low load indentations made with slowest rate and the minimum recovery (13%) showed the indentations made with highest load and rate. The reason of this behavior was analyzed from the point of view of the specific structure of the multicomponent glass and possible mechanisms of the deformation under local loading and relaxation of the induced stresses in the indentation zone. The heating, resulting in the relaxation of residual internal stresses as a whole in glass, affected the final hardness of glass, but not in the same way for all loads applied showing increased values for low load indentations and some less ones for high load indentations. This can be explained by the fact that as usual hardening may give rise to higher fragility of material. Figure. AFM cross-section profiles of 20 mN indentation made with 5 mN/s loading-unloading rate before (line 1) and after (line 2) heating. Inserted are the plan views of indentations showing cross-section lines

Rare earth doped phosphate glasses for magneto-optical devices

Bogdan Alexandru Sava¹, Mihail Elisa², Lucica Boroica¹, Olga Shikimaka³, Daria Grabco³, Victor Kuncser⁴, and Rares Medianu¹
savabogdanalexandru@yahoo.com

¹Department of Lasers, National Institute for Lasers, Plasma and Radiation Physics, Magurele, Romania

²Department of Optospintronics, National Institute for R&D in Optoelectronics INOE2000, Magurele, Romania

³Laboratory of Mechanical Properties of Materials, Institute of Applied Physics of the Academy of Sciences of Moldova, MD-2028 Chisinau, Moldova

⁴Laboratory of Magnetism and Superconductivity, National Institute of Materials Physics, 077125 Magurele, Romania

Phosphate vitreous materials were prepared and characterized from oxide system $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$, codoped with 3 mol. % Dy_2O_3 and 3 mol. % Tb_2O_3 . Bulk materials were obtained by a chemical unconventional route for raw materials obtaining with subsequent melting, refining and annealing. Mechanical stirring of the melt was applied in order to obtain a homogeneous and defects-free glass. The optimum duration and rate of the stirring were established. Annealing program was designed to preserve the desired properties of the obtained glass. The program intends both to avoid cracks and to eliminate the potential glass crystallization. Thin films, having thickness of several nm were deposited on quartz and glass substrates from targets with the above composition. Their thickness was measured during deposition and the AFM method was used to investigate the films quality. Morphology and chemical composition of the obtained bulk glasses were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy microanalysis (EDX). The EDX revealed the good homogeneity of the samples. The optical transmission in the visible range was also measured, and absorption maxima evidenced. Structural investigations on the borophosphate glasses were made by Infrared and Raman spectroscopy and meta-phosphate chains were identified as network major structural units, together with boroxol rings and BO_3 structures. The obtained glasses were investigated for the measurement of the magnetic and magneto-optic properties by using SQUID magnetometry and an adapted magneto-optical device. A diamagnetic behavior was evidenced at room temperature for the un-doped glass and paramagnetic behavior for the Dy^{3+} - and Tb^{3+} co-doped samples. The undoped glass introduces a slight positive rotation of the polarization direction of the incident light whereas the RE doping components with permanent moment (Dy^{3+} and Tb^{3+}), introduce a higher negative rotation. The rare-earth-co-doped phosphate glasses will be used for optical displacement sensors and Faraday rotators due to their magneto-optical properties.

Keywords: phosphate glass, boron oxide, rare earth co-doping, RF magnetron sputtering, AFM, SEM, FTIR, Raman, magneto-optical properties

Synthesis of Glass Ceramic-Glazes in the SiO₂-Al₂O₃-CaO-Na₂O System from Raw Materials

M. Leśniak , J. Partyka, M. Sitarz, K. Gasek
mlesniak@agh.edu.pl

AGH University of Science and Technology, Faculty of Materials Science and
Ceramics, 30-059 Kraków, Poland

Modern glazes are classified as glass ceramic composite materials because of the deliberately induced crystallization during firing. The present work show the possibility of using raw materials such as sodium carbonate (Na₂CO₃) and chalk (CaCO₃) for the production of well- covering glass-ceramic glazes, in which the only variable is the share of the silicon oxide to alumina at a constant content of other components (CaO, Na₂O,). In order to examine the real composition of the obtained glazes research on Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF) were done. These studies have shown that glazes of assumed compositions were obtained.

The effect of compositional changes on bulk crystallization and growth morphology were also studied. Wollastonite and anorthite were identified after heat-treatment. In order to determine the state of the surface (microstructure) research on the scanning electron microscope (SEM) with EDX and confocal microscopy were done. The research allowed to determine the impact of SiO₂/Al₂O₃ ratio on the structure and phase composition of glazes and the nature, and type of formed crystalline phases.

Acknowledgement

This research work has been carried out thanks to financing in the framework of NCBiR (Polish National Research and Development Committee) program PBS1/B5/17/2012 and N N508 477734

The use of experimental bending tests to more accurate numerical description of TBC damage process

Tomasz Sadowski¹, Przemysław Golewski¹
sadowski.t@gmail.com

¹Faculty of Civil Engineering and Architecture, Lublin University of Technology,
Nadbystrzycka 40, 20-618 Lublin, Poland

Thermal barrier coatings (TBCs) have been extensively used in aircraft engines to protect critical engine parts such as blades and combustion chambers, which are exposed to high temperatures and corrosive environment. The blades of turbine engines are additionally exposed to high mechanical loads. These loads are created by the high rotational speed of the rotor (30 000 rot/min), causing the tensile and bending stresses. Therefore, experimental testing of coated samples is necessary in order to determine strength properties of TBCs.

Beam samples were used in this studies, with dimensions 50x10x2 mm. TBC system consisted of 150 μ m thick bond coat (NiCoCrAlY) and 300 μ m thick top coat (YSZ) made by APS (air plasma spray) process. Samples were tested by four-point bending test with various loads. After bending tests, the samples were subjected to microscopic observation to determine the quantity of cracks and their depth.

The above mentioned results were used to build numerical model and calibrate material data in Abaqus program. Brittle cracking damage model was applied for the TBC layer, which allows to remove elements after reaching criterion. Surface based cohesive behavior was used to model the delamination which may occur at the boundary between bond coat and top coat.

Keywords: *thermal barrier coating system, brittle cracking, bending test*

Preparation of Na₂O-ZnO-B₂O₃-P₂O₅ glasses and their luminescent properties

Soichiro Kudo, Kiyoshi Itatani
itatani@sophia.ac.jp

Department of Materials and Life Sciences, Sophia University, Tokyo 102-8554, JAPAN

A white light emitting diode (LED) is an attractive illumination source, compared to the case of fluorescent lamp, because it has long life time, energy consumption saving, and environmental-friendly characteristics. Recently, some problems arose regarding the degradation of organic resins used for the blue LED with capacity enlargement. One of the promising candidates may be the inorganic glasses, instead of organic resins, because the heat resistance temperatures are generally much higher than those of resins. The present research was conducted in order to examine the properties of glasses in the Na₂O-ZnO-B₂O₃-P₂O₅ system (general formula: (50-x)Na₂O·xZnO·5B₂O₃·45P₂O₅; 10 ≤ x ≤ 40) and to check the possibility to emit the light, due to the addition of rare earth elements.

The glasses in the Na₂O-ZnO-B₂O₃-P₂O₅ system were prepared by melting the mixtures with desired amounts of NaH₂PO₄, ZnO, H₃BO₃, H₃PO₄ (85%) and Eu₂O₃ (activator) at 1100°C, and then by quenching the melts to the room temperature. The glass transition temperature (T_g) was checked by differential thermal analysis (DTA). The crystalline phases were checked by X-ray diffractometry (XRD), whereas the quantities of components were conducted by X-ray fluorescence analysis (XRF). Furthermore, the excitation and emission spectra were recorded by spectrophotometry.

The transition temperature (T_g) of (50-x)Na₂O·xZnO·5B₂O₃·45P₂O₅ glass measured by DTA increased from 311 to 355°C with x value (i.e., the increased amount of ZnO) from 20 to 40. The phase changes during the heating of (50-x)Na₂O·xZnO·5B₂O₃·45P₂O₅ glasses were examined by XRD. XRD patterns of 20Na₂O·30ZnO·5B₂O₃·45P₂O₅ glass (T_g = 328°C), for example, showed that the glass was kept being amorphous state, regardless of the increase in temperature up to 400°C; on further heating up to 450°C, however, NaZn(PO₃)₃ and BPO₄ were detected as crystalline phases.

On the other hand, the dissolution test, which was conducted by immersing the glasses into the water at 25°C for 1 h, showed that the noted water resistance was found when x values were 30 or more. Typical excitation and emission spectra of the glass with Eu²⁺ activator addition (x = 30) are shown in Fig. 1, together with emitting appearance. The glass emitted the reddish orange light at the peak wavelength of 614 nm, due to the excitement at 218 nm.

Overall, 20Na₂O·30ZnO·5B₂O₃·45P₂O₅ glass was found to possess excellent water resistance and low transition temperature, and emit the reddish orange light, due to the Eu²⁺ addition.

Keywords: glass transition temperature, rare earth activator, luminescence, reddish orange emission

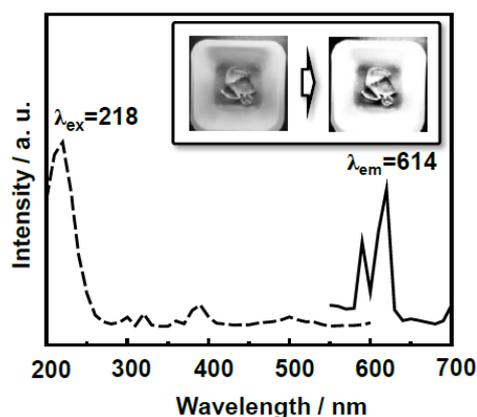


Fig1. Excitation and emission spectra of Eu²⁺-doped 20Na₂O·30ZnO·5B₂O₃·45P₂O₅ glass and its emitting appearance.

Phosphor in glass based on lead silicate glassy matrix for white LEDs

V.A. Aseev¹, Y.A. Nekrasova¹, N.V. Nikonorov¹, E.V. Kolobkova¹, J.V. Tuzova¹, O.A. Usov².
aseev@oi.ifmo.ru

¹ University ITMO St. Petersburg, Russia

² Ioffe Physical-Technical Institute of the RAS, St. Petersburg, 194021 Russia

White light-emitting diodes (LEDs) have attracted considerable attentions now due to promising features such as low energy consumption, long lifetime, small size, fast switching, as mercury free nonpolluting environment, so have a great perspective for applications in display backlights, transport and general lighting, advanced communication technique, etc.

For fixing powered phosphor on a chip usually use silicone resins. But these materials are unstable to UV exposure and temperatures above 150°C. Degradation of resins result to dramatically decreasing of WLED efficiency due to induced absorption. Inorganic materials, like glasses and ceramics, are more stable as polymer binders. For instance, thin transparent ceramic plates based on $Y_3Al_5O_{12}:Ce^{3+}$ used as a phosphor for making WLED. But sintering process is difficult and therefore results in a high cost ceramics. Glassceramics are heterophase composite materials, usually consisting of a glassy matrix (glass phase) and micro-or nano-sized dielectric crystal distributed in it. These materials provide stable to UV and temperature phosphors environments, but it is difficult to control crystallization process of phosphor, and it is possible only in a limited number of glass-forming systems.

The other type of perspective material for phosphors is phosphor in-glass (PiG). It is a simple mixture of typical commercial phosphor and glass powders (or frits). After a heat treatment, glass powders can be formed into a stable matrix for the phosphors through the viscous sintering process. The sintering temperature can be considerably lower (~600 °C) than those for phosphor ceramic sintering processes. In present work, we report $SiO_2-PbO-PbF_2-AlF_3$ glass systems as silicate glass frit materials. Sample with different glass to $YAG:Ce^{3+}$ phosphor ratios were prepared by sintering at different temperatures. Powders were pressed into disks and heat-treated at different temperatures and time durations. The spectral and luminescent properties of these PiG samples have been investigated to define the relationships between light conversion efficiency, composition and structures. Optical properties of the phosphor have been investigated. It was shown that the optical properties of WLED based of such material can be easily adjusted by changing thickness of phosphor, ratio of glass to phosphor and concentration of dopants. It was demonstrated that the new phosphor is very attractive medium for fabrication the phosphor-converted white LEDs.

Keywords: LED, Phosphor in glass, $YAG:Ce^{3+}$, glass

Influence of ZnO content on the crystallization behavior of Zn_2SiO_4 in glazes

Katarzyna Gasek¹, Jerzy Lis¹, Janusz Partyka¹
gasek@agh.edu.pl

¹ AGH University of Science and Technology, Faculty of Material Science and Ceramic, Department of Ceramic and Refractory Materials, al. Mickiewicza 30, 30-059 Kraków, Poland

The unique effect in crystalline glazes are realized by crystallization of willemite. Willemite is a zinc silicate having formula Zn_2SiO_4 . The size, shape and number of the crystals depends on the composition of the glaze and firing conditions. Crystalline glazes contain a high amount of ZnO in the composition.

In this paper glazes of the SiO_2 - Al_2O_3 -CaO- K_2O system with addition of ZnO were studied. The influence of zinc oxide content on formation of willemite crystal in glazes was tested. A minimal amount of ZnO obligated to form Zn_2SiO_4 crystals in glazes was also determined. In researches prepared some glazes differ only the content of ZnO and fired under the same conditions. The powder of glazes and glazing samples with commercial ceramic body were tested. A main crystalline phase of glazes – willemite and other phases of the fired glazes found by using X-ray analysis (XRD). The morphology and number of Zn_2SiO_4 crystals were investigated using optical microscopy. The microstructure of crystalline glazes were analyzed with a scanning electron microscopy (SEM).

Keywords: *crystalline glaze, willemite, zinc silicate, ZnO addition, crystallization, crystals,*

Effect of Oxides of Alkali Metals and Alkali Earth Metals Molar Ratio on the Surface Parameters of Porcelain Glaze

Partyka Janusz, Gasek Katarzyna, Gajek Marcin
gasek@agh.edu.pl

Faculty of Material Science and Ceramics, Department of Ceramics and Refractories, AGH University
of Science and Technology, Krakow, Poland

The performance characteristic of porcelain glazes are strongly dependent on the quality of the surface. The main investigated properties of glaze surface properties are smoothness, glossy and whiteness. The research was carried on porcelain type glaze for firing temperature 1220-1230°C. The glazes were characterized by a constant molar ratio of $\text{SiO}_2 / \text{Al}_2\text{O}_3$ and constant molar sum of the oxides of alkali metals and alkali earth metals with various their molar ratios. The research allowed to determine the relationship between the glaze surface parameters and the type and amount of introduced cations.

Keywords: *ceramic glaze, surface parameters, smoothness, glossy, alkali metal oxides, alkali earth metal oxides, molar ratio*

Photofragmentation and Photoionisation of Silver Nanoparticles in Photo-Thermo-Refractive Glass

Ignatiev A.I., Ignatiev D.A. and Nikonorov N.V.
ignatiev@oi.ifmo.ru

Saint-Petersburg National Research University of Information Technologies, Mechanics and Optics,
4 Birzhevaya line, St. Petersburg, 199034, Russia

Photo-thermo-refractive (PTR) glasses are perspective material for highly efficient volume phase holograms recording. PTR-glasses allow to precipitate silver molecular clusters (SMCs) under UV irradiation and metallic nanoparticles possessing surface plasmon resonance (SPR) in local area of glass host by photo-thermo-induced crystallization. Also these silver nanoparticles can play a role of nucleation centers for secondary crystalline phases (NaF, AgBr) precipitation.

Two types of PTR glasses (chloride and bromide) of approximate composition $15\text{Na}_2\text{O} - 4\text{Al}_2\text{O}_3 - 5\text{ZnO} - 70\text{SiO}_2$ (mol%) doped with Ag_2O , CeO_2 and Sb_2O_3 have been synthesized in the present work. Silver in the origin PTR glasses is situated in the form of silver ions Ag^+ and molecular ions Ag_n^{m+} . The silver nanoparticles with silver halide shells were precipitated with the use of UV radiation into Ce^{3+} absorption band and following heat treatment at temperature above glass-transition ($T_g = 495^\circ\text{C}$) [1]. The formation of silver nanoparticles with NaBr-AgBr and NaCl-AgCl shells resulted in an appearance of strong absorption band in the spectral range of 420-490 nm corresponding with plasmon resonance of the silver nanoparticles. The SEM measurement has shown that silver nanoparticles diameter achieved 5-10 nm. The bleaching of the complex silver nanoparticles was performed by the second harmonic ($\lambda = 532$ nm) of pulse YAG:Nd laser (pulse duration of 10 ns, pulse repetition rate of 10 Hz and pulse energy of 0.1 J). The diameter of irradiated zone was 3.5 mm.

The photodestruction process of silver nanoparticles in PTR-glassceramics as a function of pulse energy, exposure dose and halogenide surroundings of silver nanoparticles were investigated. It was shown that during the irradiation the silver nanoparticles absorption band decreased depending on the exposure dose and can be totally disappeared. Silver nanoparticules in glass host as well as inside of nanocrystalline phase are destructed. The halogenide surroundings effected on a kinetic of photodestruction. The photodestruction kinetic of silver nanoparticles has bleaching threshold and nonlinearly depends on pulse energy. We made a conclusion that the pulse laser irradiation resulted in photofragmentation of the nanoparticles with creation of atoms, clusters, and small particles as well as photoionisation of atoms with creation of silver ions. The technology allowed us to control the size of the silver nanoparticules in glassceramics and create the phase holograms in visible and near IR range (400-3000 nm).

Keywords: *silver nanoparticles, photo-thermo-refractive glasses, photofragmentation, photoionisation, pulse laser radiation,*

Optical properties of fluorine phosphate glasses doped with (CdS)_n (CdSe)_n, (PbSe)_n and (PbS)_n molecular clusters and quantum dots

E. Kolobkova, N. Nikonorov, A. Sidorov, T. Shakhverdov
kolobok106@rambler.ru

University ITMO St. Petersburg, 199034, Russian Federation

Optical composite materials with CdS, CdSe, PbSe and PbS quantum dots are widely used in optics and photonics. Such materials possess luminescent properties in visible (CdS, CdSe) and has non-linear optical properties in near IR (PbSe and PbS) spectral region. The cadmium and lead chalcogenide quantum dots in glasses typically are prepared during heat treatment of glass, containing cadmium or lead and chalcogenide ions, at temperature higher than glass transition temperature (T_g). Thermal diffusion of ions leads to the formation and growth of quantum dots (QDs) in the glasses. The variations of heat treatment temperature and duration of heating make possible to changes the sizes of the QDs in a wide range. It is evident, that during the formation and growth such structures passed the stage, when their sizes are less than 1 nm and they do not possess semiconductor properties. This stage corresponds to the existence of the cadmium or lead chalcogenide compounds in a glass in a form of the subnanosize molecular clusters (MCs). The optical properties of the molecular clusters are considerably different from the properties of QDs.

In our experiments, we observed the intense luminescence in a visible region in as-prepared (before thermal treatment) fluorophosphates glasses (FPG) with Cd, Pb, Se and S ions. This indicates the presence of (PbSe)_n, (CdS)_n, (CdSe)_n and (PbS)_n MCs in the initial glasses, which play the role of crystallization centers for quantum dots during heat treatment. The goal of our present work is the study of luminescence properties of fluorophosphate glasses with (CdS)_n (CdSe)_n, (PbSe)_n and (PbS)_n MCs before quantum dots formation and of luminescence properties of the CdS, CdSe, PbSe and PbS QDs. The influence of heat treatment on MCs and QDs luminescence was studied.

It was shown experimentally, that fluorophosphates glasses, containing Pb, Cd, Se and S ions possess strong luminescence in a visible spectral region when excited by near-UV radiation. This luminescence is connected with formation of the (PbSe)_n, (CdSe)_n, (CdS)_n and (PbS)_n MCs and CdS, CdSe QDs in a glass. The heat treatment at temperatures less than glass transition temperature results in the increasing of the luminescence intensity. During the heat treatment at glass transition temperature this molecular clusters play the role of crystallization and growth centers for CdSe, CdS, PbSe and PbS QDs. Fluorophosphates glasses, containing PbSe and PbS QDs possess strong luminescence in a NIR spectral region when excited by radiation of visible and NIR region. With growth of this QDs from 2 to 15 nm luminescence band shifted from 1000 to 2500 nm. New luminescent fluorophosphates glasses with MCS and QD are promising as phosphors in photonic devices, down-converters of solar radiation in solar cells, and in luminescent fiber temperature sensors and dosimeters of UF radiation.

Modified glass surfaces with advantageous properties: preparation and characterization

Emőke Albert¹, Pierre-Antoine Albouy², André Ayrat³, Péter Basa⁴, Gabriella Csík⁵, Ágnes Suhajda⁶,
Zoltán Hórvölgyi¹
emokealbert@mail.bme.hu

¹Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1111 Budapest, Hungary

²Paris-Sud University, 91405 Orsay, Paris, France

³European Membrane Institute, Montpellier 2 University, 34095 Montpellier, France

⁴Semilab Semiconductor Physics Laboratory Co. Ltd., H-1117 Budapest, Hungary

⁵Institute of Biophysics and Radiation Biology, Semmelweis University, H-1094 Budapest, Hungary

⁶Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics, H-1111 Budapest, Hungary

The importance of nanostructured thin coatings has recently increased. Properties and possible applications of these films are determined by their structure and chemical composition.

Coatings prepared by sol-gel techniques on glass substrates can lead to

- improved light transmittance, i.e. antireflectivity (mesoporous silica coatings)
- water repellence (surface modified silica coatings)
- self-cleaning and antibacterial behaviour (semiconductor composite coatings).

We will report about the study of TiO₂ and SiO₂ coated glass surfaces having the aforementioned properties. Coatings were deposited onto glass and (in some cases) silicon substrates by the dip-coating method. Porous SiO₂ and TiO₂ films were fabricated by using non-ionic (Pluronic PE 10300, Pluronic P 123) and cationic (CTAB) surfactant templates. Optical properties of coatings were determined by UV-Vis spectroscopy and ellipsometric porosimetry. The structure of the coatings was investigated by scanning electron microscopy and by X-ray diffraction, the composition was analysed by X-ray fluorescence and Rutherford backscattering spectrometry methods. Water repellence was characterized by contact angle measurements and antibacterial activities were studied against E. coli in dark and in visible light by different methods. The recently obtained results will be summarized in our presentation.

Keywords: *sol-gel coating, glass substrate, improved light transmittance, self cleaning surfaces, water repellence, photocatalytic property, antibacterial behaviour*

Acknowledgements

The authors thank E. Hild, A. Deák, N. Nagy, V. Rouessac, D. Zámbo, Zs. Zolnai, R. Barna, A. Bánkúti, T. Becsei, Z. Horváth, R. Jancsek, É. Kunsági-Máté, Zs. Molnár, K. Pázsai, R. Szabó for their help in this work.

The financial support of the New Széchenyi Plan (TÁMOP-4.2.1/B-09/1/KMR-2010-0002) and of the National Development Agency (Hungarian-French Bilateral Co-operation, PHONOSEL, TÉT_11-2-2012-0008 and Hungarian-Romanian Bilateral Co-operation, SOLGELCOR, TÉT_12_RO-1-2013-0011) is gratefully acknowledged.

Emőke Albert's research work was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP-4.2.4.A/ 2-11/1-2012-0001 "National Excellence Program".

Frame Bulk Porous Material With the Controllable Geometrical Parameters of Structure and Surface Nanolayer

Sidelnikova Olga N.
ol_sideln@mail.ru

*Institute of Solid State Chemistry and Mechanochemistry,
Novosibirsk, Russia*



The one/multi component frame bulk porous material with holes uniformly allocated on all surface is considered in report. Such material may be useful in chemical processes with participation and formation of the gaseous products and requires the gas/liquid permeability of solid state material. The substantial surface area of material may be available for reaction (catalytic, electrochemical or others) and it may be achieved also the better material's properties (corrosion resistance, mechanical stability, others). The material modification can be realized by precise physical/chemical methods (for instance, chemical or electrochemical etching, laser technology, lithography). It was calculated [1] that the material's specific surface area (thickness h and density ρ) with equidistant cylindrical holes (radius r) net is equal: $(S_1)_{\text{spec}} = 2/\rho * [1/h + (\pi/(9 - \pi))/r] \sim 2/\rho * (1/h + 0.536/r)$ (**Eq. 1**). The relation of the specific surface area of the material with equidistant cylindrical holes net to the initial specific surface area of the material without holes is expressed by **Eq. 2**: $(S_1)_{\text{spec}}/(S_{\text{in}})_{\text{spec}} = 1 + \pi/(9 - \pi) * h/r \sim 1 + 0.536 h/r$.

It has been made also consideration of frame bulk porous material with deposited nanolayer (submonolayer, monolayer or multilayer); it led to **Eq. 3**: $(S_1)_d/S_{\text{in}} = S_1/S_{\text{in}} * (1 + \pi * N_d^*)$, where $(S_1)_d/S_{\text{in}}$ is the relation of the result surface area of the bulk porous material with nanolayer to the initial surface area of the material without holes and nanolayer; S_1/S_{in} - the relation of the result surface area of the bulk porous material without nanolayer to the initial material' surface area without holes and nanolayer; N_d – monolayers' number. If the particles in the layer occupy the part D of the material's surface area then the relation $(S_1)_d/S_{\text{in}}$ is expressed in **Eq. 4**: $(S_1)_d/S_{\text{in}} = S_1/S_{\text{in}} * (1 + 4D)$, for $D = 0.1$ $(S_1)_d/S_{\text{in}} = S_1/S_{\text{in}} * 1.4$, for $D = 0.2$ $(S_1)_d/S_{\text{in}} = S_1/S_{\text{in}} * 1.8$, for $D = 0.4$ $(S_1)_d/S_{\text{in}} = S_1/S_{\text{in}} * 2.6$, for $D = 0.6$ $(S_1)_d/S_{\text{in}} = S_1/S_{\text{in}} * 3.4$.

References

1. Sidelnikova O.N., Zacharov M.A., Salanov A.N. Patent RF № 2336370, 2008.

On Advantage of Scattering Glass Material Modified by Surface Ion Exchange for Energy Efficient Use in Technical and Decorative Lighting

Olga Nikolaevna Sidelnikova¹, Gerge Alekseevich Pozdnyakov², Aleksey Nikolaevich Salanov³
ol_sideln@mail.ru

¹ Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of Academie of Science

² Khristianovich Institute of Theoretical and Applied Mechanics, Siberian Branch of Academie of Science

³ Borekov Institute of Catalysis, Siberian Branch of Academie of Scien

The present research data are related to soda lime silica glass material modified by the surface ion exchange process /1, 2/. The optical properties of the glass material were measured conjointly by Sidelnikova O.N. (ISSCM) and Pozdnyakov G.A. (ITAM) and compared with that data related to chemically etched glass. Also the surface morphological research was carried out by Sidelnikova O.N. (ISSCM) and Salanov A.N. (BIC) using SEM method. The glass material modified by surface ion exchange is characterized by more effective simultaneous light transmission and light scattering and by more strongly pronounced spectral and angular dependences of the scattered light. A noticeably greater light intensity (up to 16 times!) was found at light propagating in the full internal reflection regime. Such optical data may be useful in technical and dcorative illuminating engineering. The presented scattering glass material may be used for manufacture of the glass production of luminaries, light screens, indicator panels, displays, decorative or technical images on glass and elements of architectural design, glass sculptures and others.

References

1. G.A. Pozdnyakov, O.N.Sidelnikova, A.N.Salanov Glass Tech.: European J. of Glass Sc. and Tech. Part A, Dec. 2010, vol. 51, N6, p.241-247. 2. O.N.Sidelnikova, G.A. Pozdnyakov, A.N. Salanov, A.N.Serkova Glass Tech.: European J. of Glass Sc. and Tech. Part A, Febr. 2011, vol. 52, N1, p. 15 - 22. ;

Thermal Insulation Properties Research of the Composite Material “Water glass- Graphite Microparticles”

Anton Ustinov¹, Eugene Pitukhin², Valeriy Gostev¹, Darya Yakovleva¹
anton-ustinov@psu.karelia.ru

¹ Physical Engineering Department, Petrozavodsk State University, Petrozavodsk 185910, Russian Federation

² Department of Mathematics, Petrozavodsk State University, Petrozavodsk 185910, Russian Federation

Currently one of the most important problems is to provide materials and coatings designed to reduce heat loss and resistant to high temperatures. One way of addressing this issue is the development of technology for preparation and use of composites, which after application to the surface slows down its warming up. Unlike most of the conventional composite materials is that their production process may be combined with the process of manufacture. The use of graphite as a filler justified by its high temperature and chemical resistance.

The authors developed and investigated experimentally obtained new composition material elevated temperature stability and thermal insulation properties, with the results directed towards reducing the cost of their production.

A composition consisting of graphite (42 % by weight), water glass $\text{Na}_2\text{O}(\text{SiO}_2)_n$ (50% by weight) and the hardener - sodium silicofluoric Na_2SiF_6 (8% by weight). Technology of such composition receipt is suggested. Experimental samples of the CM with filler particles (graphite) and a few microns (up to ten micrometers) in size were obtained. This is confirmed by a study of samples by X-ray diffraction and electron microscopy. The qualitative and quantitative phase analysis of the CM structure is done. Load limit values leading to the destruction of CM are identified. The character of the rupture surface is detected. In order to determine the load required for the separation of coating from the test surface of the base composition was applied to the finished wood samples (thickness 2 mm). After complete drying the samples ripped by defining the load at break cover with an accuracy of 10 N/m². The load was applied to the sample by hanging on cargo accessories - hooks. Destruction of the sample occurred along the boundary of the composite material and the substrate at the structure in the longitudinal section. Limit fixed load value was 1.22 MPa. Cracks in the samples were formed. This was confirmed by a discontinuous surface of pictures after the experiment and micrographs (electron microscope Hitachi SU 1510) surface separation (out of 10 microns and 50 microns). Dependence of the specific heat capacity and thermal conductivity on temperature at monotonic heating is obtained experimentally. Studies have confirmed the increased thermal insulation properties of the proposed composition. X-ray diffraction of samples subjected to heating to 673, K showed that the material is able to maintain the same chemical structure, confirming that it was a higher temperature resistance. CM with such characteristics can be recommended as a coating designed to reduce heat losses and resistant to high temperatures. Due to accessibility and low cost of its components the proposed material can be produced on an industrial scale.

Keywords: *composite material, thermal insulation properties, water glass, graphite filler, X-ray analysis, specific heat, thermal conductivity.*

Increasing resistance of multilayer nanocomposite coatings TiN- AlTiN - TiAlN by optimizing their architecture

Anton V. Kurochkin, Tatiana D. Kozhina
kurochkin.a.v@yandex.ru

Solovjov Rybinsk State Technical University of Aviation, str. Pushkina, 53, Rybinsk, Russia

Wear-resistant coatings are an important part of modern tool materials. The coatings are applied to the most advanced tools. Coating technology allows us to give them the characteristics needed for specific processing conditions coating effectively complements the physical and mechanical properties of the substrate of tungsten carbide.

To control machining using coated tools to solve complex optimization problem - it was necessary to relate the criteria describing the properties of the coating to the physical processes in the cutting zone.

Optimization of the proposed architecture of multilayer wear resistant nano-composite coatings TiN- AlTiN - TiAlN of solid carbide end mills used for the manufacture of parts of modern aircraft of the motor and power systems of aircraft is less affected by the deformation stress by developing mathematical models to estimate the stress-strain state of coatings. We present the study of multilayer coatings inspection to identify the most efficient architectures of multilayer coatings applied to the mono-lithic carbide end mills [1]

Keywords: *solid carbide end mills, multilayer wear-resistant nanostructured coatings, coating defects, optimization*

[1] Kurochkin A.V. Tehnicheskir osobennosti mnogofunktsional'nyh nanostrukturirovannyh pokrytii dlya rezhushhego instrumenta. Vestnik RGATA imeni P. A. Solov'eva, Rybinsk, 2010, vol. №3 (18), p. 166-172.

SESSION 6

Hetero-Modulus and Hybrid Materials

Nano Organic Compounds Embedded in Silicophosphate Thin Films for Nano Electronics

Cristina Vasiliu¹, Andreea Matei², Mihai Elisa¹, Raluca Iordanescu¹, Ionut Feraru¹,
Ana Emandi¹, Raluca Iordanescu¹, Iulian Ionita³
icvasiliu@inoe.inoe.ro

¹ National Institute for Optoelectronics -INOE 2000, Optospintronics

² National Institute for Laser, Plasma and Radiation Physics, Maple

³ University of Bucharest

The large second-order nonlinearity and high-speed response of doped organic compounds are of great interest for optical communications and high-density optical data storage. The sol-gel technique is a promising approach in the fabrication of new materials for second-order nonlinear optics. We report in the present paper on the sol-gel synthesis of SiO₂-P₂O₅ films doped with some metal azo derivatives. The precursors used for sol gel synthesis were tetraethylorthosilicate (TEOS) and phosphoric acid (H₃PO₄). The organic compound and metal salt were added under continuous stirring in the precursors' mixture. The structure of the deposited metal azo-derivatives doped thin films was examined by Fourier transform infrared spectroscopy, and atomic force microscopy and their optical properties by UV-VIS and fluorescence spectroscopy. The nonlinear optical efficiencies due to the interaction of the NLO-active chromophores with the inorganic matrix was measured using a femtosecond Ti:sapphire laser. The properties of the films were investigated and correlated with the concentration of the organic dopant and the thermal treatment temperature.

Ni/Al₂O₃ Nanocomposites as Self-healing Structural Ceramics

Makoto Nanko¹, Hai Vu Pham¹ and Daisuke Maruoka^{1,2}
nanko@mech.nagaokaut.ac.jp

¹ Department of Mechanical Engineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan

² Department Material Science and Chemical Engineering, Yokohama National University, Yokohama, Kanagawa 240-8501, Japan

Nanocomposites consisting of ceramic matrix and metallic nano-particle dispersion are expected as advanced structural materials with high mechanical strength and excellent fracture toughness even at high temperatures. Our research group has discovered some of the metal/ceramic nanocomposites with autonomous crack-healing function at high temperatures in oxidizing atmosphere. In particular, Ni/Al₂O₃ nanocomposites, typically 5 vol% Ni, can be fabricated easily with excellent crack-healing performance and excellent mechanical properties. In Ni/Al₂O₃ system, the oxidation product, NiAl₂O₄, is formed in cracks because of significant cation diffusion passing through the grain boundaries of Al₂O₃ matrix. Filling up of NiAl₂O₄ in surface cracks can reduce stress concentration at the crack tips. As a result, mechanical strength of Ni/Al₂O₃ can be recovered up to the level of mechanical strength of as-polished samples.

Ni/Al₂O₃ nanocomposites are oxidized at high temperatures in oxidizing conditions. Oxidation of Ni particles in Ni/Al₂O₃ nanocomposites degrades their crack-healing performance. In oxidizing atmosphere at high temperatures, Ni dispersoid in the nanocomposites is oxidized with Al₂O₃ matrix into NiAl₂O₄ from the composite surface. Growth of the oxidized zone, consisting of NiAl₂O₄ grains in Al₂O₃ matrix, follows the parabolic manner. Oxidation rate of Ni/Al₂O₃ nanocomposites can be decreased by doping Y or Si into Al₂O₃ matrix.

In healing cracks with 200 μm in depth introduced by the Vickers indentation, mechanical recovery is achieved with heat treatment at 1200°C for 1 h in air. Depth of the oxidized zone is approximately μm. Crack-healing rate of Ni/Al₂O₃ nanocomposites is larger than oxidation rate. The life-time of crack-healing function of Ni/Al₂O₃ nanocomposites is expected to be long taking account of high temperature oxidation.

Keywords: Ni, Al₂O₃, NiAl₂O₄, nanocomposites, crack-healing, oxidation

Investigation of structure and characterizations of zirconium tungstate with unique thermal properties

Elena Dedova¹, Vladimir Shadrin², Victoria She², Alexander Gubanov³ and Sergey Kulkov^{1,2}
Isdedova@yandex.ru

¹Institute of Strength Physics and Materials Science SB RAS, 634021 Tomsk, Russia

²Tomsk State University, 634050 Tomsk, Russia

³Nikolaev Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russia

Zirconium tungstate as materials with anomalous thermal properties is the perspective material due to a isotropic negative coefficient of thermal expansion (CTE), $\alpha = -9.6 \cdot 10^{-6} \text{C}^{-1}$, from very low (-273°C) to high (770 °C) temperatures. Composites with a negative CTE materials may become very useful in various applications, for example, an introduction of the ZrW_2O_8 particles as reinforcement element into metal matrix allowed to obtain the composites with high strength properties due to difference of values of coefficients of thermal expansion of matrix and reinforcement: calculations showed that the internal compression stresses generated by the difference of values of the CTE may increase up to 2 GPa compared with Orowan strengthening $\Delta\sigma \sim 20$ MPa.

The ZrW_2O_8 was prepared by low temperature decomposition of precursor obtained by hydrothermal method. The starting components for preparing the precursor were aqueous $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and HCl. The hydrothermal reaction occurred at 160 °C for 36 h. The product $\text{ZrW}_2\text{O}_7(\text{OH}, \text{Cl})_2 \cdot 2\text{H}_2\text{O}$ was repeatedly washed with distilled water, filtered and dried at 110°C. Finally, when being heated at 570 °C for 1 h the $\text{ZrW}_2\text{O}_7(\text{OH}, \text{Cl})_2 \cdot 2\text{H}_2\text{O}$ was transformed into ZrW_2O_8 .

The morphology of the ZrW_2O_8 was represented as the rod-shaped particles having a private block structure. The average size of this blocks was changed from 20 to 50 nm. The average transversal size of rod-shaped particles was varied from 30 to 700 nm, the average length size was varied from 0.5 to 5µm. The ZrW_2O_8 synthesized was kinetically stable from 25 to 540 °C. The crystal structure of ZrW_2O_8 was studied. The ZrW_2O_8 synthesized demonstrated a negative thermal expansion behavior from 25 to 750 °C.

Keywords: zirconium tungstate, negative thermal expansion, hydrothermal synthesis

Numerical Investigation of the Dependence of Elastic and Strength Properties of Ceramics Based on Metal Nanocrystal Oxides on Partial Concentrations of Pores with Different Size in its Structure

Igor Konovalenko, Alexey Smolin, Vladimir Promakhov, Ivan Konovalenko, Sergey Psakhie
ivkon@ispms.tsc.ru

Institute of Strength Physics and Materials Science of the Siberian Branch of the Russian Academy of Sciences, 634021 Tomsk, Russia

The pore structure of the ceramic material is characterized by the presence in it of pores with different sizes. Pore size distribution function of these materials contains several (in the simplest case of two) maxima. The height and width of each maximum determine a fraction of pore space corresponds to pores with the proper size.

Thus, the materials with a bimodal pore size distribution function and with a certain value of the total porosity can be characterized by a great number of combinations of pore structure parameters: volume ratio of pore space corresponding to the pores of the first and second peak of the function. In this aspect, said material is no longer just a porous body, but it is a construction. The mechanical behavior and properties of this construction are determined by the specified parameters of its structure. In practice, the combination of the parameters of the pore structure and mechanical properties of the material largely determine the scope of its functional application. It does knowledge about the mechanical properties of material in the entire range of these pore structure parameters very actual and required. Thus, in this paper, a numerical study of the dependence of the strength and elastic properties of ceramic materials on the fraction of pore volume corresponding to pores of the second maximum of the pore size distribution function in the total porosity of material was carried out.

Calculations were based on multiscale approach, developed in the framework of the of movable cellular automaton method (MCA). Plane MCA-model of ceramic $ZrO_2(Y_2O_3)$, with a pore size comparable with the grain size and bimodal pore size distribution function was developed. Material with round pores was considered. On the basis of computer calculations an analytical estimation for numerical dependence of strength and elastic properties of material under compression loading on its total and partial porosities, corresponding to pores with different size, was found. It was shown that the strength of brittle materials, containing pores of two different sizes, is defined as the value of total porosity and the value of partial porosities, corresponding to one of the maxima of the of pore size distribution function. The difference in the strength of such materials with the same value of total porosity, but with different number of pores with different size can be up to 50%. Effective elastic modulus of the material are determined only by the value total porosity.

This study was partially supported by the Russian Foundation for Basic Research, Project № 12-08-00379-a and by the Grant of the President of the Russian Federation for the state supporting young Russian scientists, Project MK- 5883.2014.8.

Keywords: *ceramics on the basis of metal oxides, mechanical properties, pores with diifferent size, computer simulation, movable cellular automaton method*

Hetero-structure Formation and Properties of SnO₂-TiO₂ Ceramic Composites via Spinodal Phase Separation

Tohru Sekino^{1,2}, Shun-Ichiro Tanaka², and Takafumi Kusunose³
sekino@tagen.tohoku.ac.jp

¹Institute of Scientific and Industrial Research, Osaka University, Osaka 567-0047, Japan

²IMRAM, Tohoku University, Sendai 980-8577, Japan

³Department of Advanced Materials Science, Kagawa University, Kagawa 761-0396, Japan

SnO₂-TiO₂ binary ceramic system is well known to exhibit a solid solution over 1430°C and to form a spinodal phase separation by annealing within its immiscibility region, which exhibits characteristic lamellar structure. Such self-organized composite structure has a large heterogeneous interface area within its bulk form. Therefore it can be thought that the hetero-interface might act as “functional interface” in ceramic materials. In this research, we have challenged multidisciplinary controls of spinodal-originated composite and materials electrical properties of the hetero-modulus oxide system, and their microstructures and electrical resistivity were investigated.

Trivalent iron (Fe³⁺) was selected for the control of the spinodal phase separation in SnO₂-TiO₂ system, and was doped to the binary oxides via solid-state reaction sintering. Fe₂O₃ powder of 2 to 5 mol% was added to equimolar (1:1) mixture of SnO₂ and TiO₂, and the mixtures were pressureless sintered at 1300 to 1450°C under an air atmosphere. The samples were then ground and polished to form discs with 13 mm in diameter and 2 mm in thickness. Microstructure was analyzed by scanning and transmission electron microscopy (SEM and TEM) and electron probe micro-analyzer (EPMA). The phase development was carried out by X-ray diffraction method (XRD). Electrical resistivity of the composites was measured by van der Pauw method at room temperature.

Sintering below 1330°C, it was found that the sample was mainly composed from SnO₂ and TiO₂ rich grains, whereas above 1360°C, typical lamellar structure started to form even after the one-step sintering, which phenomenon could not be observed for the non-doped system. Thus it is thought that Fe accelerate the spinodal phase decomposition in the SnO₂-TiO₂ system.

From detailed SEM and EPMA analyses, it was considered that the lamellar was formed by the Ti diffusion to the SnO₂ grains at low-temperature and then mutual-diffusion of the Ti and Sn started to complete the lamellar formation at higher sintering temperature. Electrical resistivity of the composite depended on the phase development, and decreased with the lamellar formation. Detailed microstructural development and electrical properties of the self-organized SnO₂-TiO₂ ceramic composites will be discussed.

Keywords: ceramic, composites, oxides, semiconductors, dope, spinodal, phase separation

Intermediate Layer Formation between Inclusions and Matrix During Composite Synthesis at Given Temperature and Pressure

Knyazeva A.G.^{1,2}, Lurie S.A.³, and Solyaev Yu³
anna-knyazeva@mail.ru

¹Tomsk Polytechnic University, 634050, Tomsk, Russia

²Institute of Strength Physics and Material Science SB RAS, 634021, Tomsk, Russia

³Institute of Applied Mechanics RAS, 125040, Moscow, Russia

The intermediate layer between inclusions and matrix determines the mechanical and physical properties of composites. To investigate the kinetics phenomena going near interface it is necessary to solve the problem on new phase formation and evaluate the stresses appearing in diffusion - reaction zone. When unidirectional fiber composite is synthesized, we can formulate the problem in general case in cylindrical coordinate system. The intermediate layer formation occurs near by the vicinity of individual fiber of given initial size. The problem on mechanical equilibrium of fiber in environment matrix is solved in term of quasistationary thermoelastic diffusion theory with the conditions of ideal contact between initial substances and growing new layer. The concentration distributions follow from reaction-diffusion problem. The concrete diffusion problem formulation depends on the system under study. When the composite on the base of aluminum with fibers of aluminum oxide is formed, the intermediate layer forms mainly in the fiber direction. When the composite is formed from Si-C fiber and titanium matrix, the intermediate layer growths mainly in the direction of the matrix. In any case, the diffusion – reaction layer is very narrow in comparison with fiber radius. That allows simplifying the diffusion-kinetic problem and constructing its analytical solution.

As a result, we obtain the thickness of intermediate layer, concentration distributions and stresses and strains for different time moments varying the input data.

Keywords: *composite synthesis, intermediate layer, diffusion, chemical reaction, fiber, stresses, analytical solution, phases and elements distribution*

Improving adhesion strength of thermally sprayed ceramic coatings on CFRP substrates

Septimiu Popa, Rainer Gadow
septimiu.popa@ifkb.uni-stuttgart.de

Institute for Manufacturing Technologies of Ceramic Components and Composites, University of Stuttgart, Stuttgart D-70569, Germany

Carbon fiber-reinforced plastic (CFRP) bear a great potential for aircraft and automobile applications due to its light weight, high specific stiffness and high specific strength. Despite those qualities, the CFRP matrix lacks the ability to withstand high temperatures which can lead to component failure if exposed to such environments. To protect the CFRP panels from high thermal loads it is crucial to apply a protective coating. This is realized through a thermo-kinetic spray process. These high energetic deposition processes enable to apply high meltable metallic and ceramic coating with melting points above 2000 °C. These high process temperatures in combination with the polymeric CFRP-substrate require a detailed knowledge on processing and cooling to prevent thermal degradation and minimize residual stresses. A main difficulty is the fabrication of the functional layer directly on the CFRP substrate, so an metallic interlayer is applied by plasma spray or twin wire arc spray process. The main challenge is to achieve satisfying adhesion strengths at the interface between coating and CFRP surface, to cope with mechanical stress without coating failure. The present work focuses on ways to improve the adhesion strength through surface treatment prior coating. CFRP samples are treated on one hand mechanically (grid blasting) and on the other hand through laser structuring. After coating the adhesion strength is measured by pull-off test. The results are compared to evaluate the efficiency of the applied surface treatments.

Keywords: *Adhesion testing, carbon fiber reinforced plastic (CFRP), aluminum coating, interlayer, atmospheric plasma spray, twin wire arc spray.*

The relationship between properties and structure of multiwall carbon nanotube contained polymer nanocomposites

Andrea Adamné Major, Karoly Belina
major.andrea@gamf.kefo.hu

Department of Material Technology, Kecskemét College, Kecskemét 6000, Hungary

Nowadays polymers have important rule in the field of technological researches. They are used instead of metals or ceramics. The other type of interesting materials is the carbon nanotubes. They are well known because of their specific properties. The most interesting features can be reached when we produce nanocomposites. Polymer nanocomposites consist of two different part: the polymer matrix and the nanoparticle. The nanoparticle is often the carbon nanotube.

During our experiments we used different polymers as matrix material and multiwall carbon nanotube. Concentration series were produced by a new type of mixer called IDMX mixer. The mechanical, burning properties and the crystallization of the nanocomposites were investigated. We also studied the structure of the nanocomposites. We have found relationship between the properties and the structure of the multiwall contained polymer nanocomposites.

Keywords: *polymer, carbon nanotube, mechanical properties, thermal properties, burning properties, structure*



Figure 1. IDMX mixer

SESSION 7

Light-Weight Metals and Alloys

Bearing capacity of C-shaped cold-bent notched profile members

Nikolay I. Vatin¹, Tatiana Nazmeeva²

¹vatin@mail.ru, ²naztv@mail.ru

^{1,2}Saint-Petersburg State Polytechnical University, 195251 Saint-Petersburg, Russia

Nowadays in Russia we have a steady rising erection volume of pre-fabricated energy-efficient buildings based on cold-bent thin-walled galvanized steel profile with economic use of limited fuel and power resources. Building system of this type is a system of cold-bent steel profile framework filled in with effective heat retainer and then jacketed with sheet materials. Separate elements of the framework are joined in one load-bearing structural element (panel) with the help of guide casings and sheets. Members in a frame building panel undergo eccentric compression with biaxial eccentricity.

Cold-bent c-shaped profile is used for interior panel members, and cold-bent nonequilateral notched C-profile is used in exterior panels. Lengthwise notches made chequerwise in the profile walls increase the distance of heat flow and decrease heat conductivity and eliminate cold bridges that is why the profile is called "thermal profile".

Cold-bent profile made by cold bending requires alternate approach when engineering structures are designed and maintained. The approach means thin walls' and the profile special form' impact on the bearing capacity and stability of the structures should be taken into account. In spite of the wide use of cold-bent C-shaped notched profile in building frameworks, we see lack of information on how the notches influence the bearing capacity and stability of structures. There are no official normative documents on calculation and designing of cold-bent notched profile structures.

The purpose of the work is to find ultimate bearing capacity and to study stress-strain behavior of compressional cold-bent notched C-shaped profile members as well as comparison study of their work and that of cold-bent solid section C-shaped profile members. Bearing capacity value is influenced by value of eccentricity that increases bimoment, and reduced area, as well as some initial imperfections.

We carry out theoretical and experimental investigations on global buckling and bearing capacity of steel members of C-shaped notched profiles of different cross-sections area. The authors of the article developed two testing beds C-12 (1200mm/20t) and B-50 (2200mm/50t) to carry out experimental investigation.

Numerical solution of stability of a thin-walled member made of C-shaped profile was received during the numerical simulation done in PLM Femap 10.1 Nastran.

Keywords: cold-bent profile, local buckling, resistive-strain sensor, thin-walled members, numerical simulation, bearing capacity

Metal matrix composites based on A356 aluminum alloy reinforced by diamond nanoparticles

Anton Khrustalyov¹, Sergey Vorozhtsov^{1,2}, Sergey Kulkov^{1,2}, Dmitry Eskin³
tofik0014@mail.ru

¹ National research Tomsk state university, Lenin str., 36, Tomsk, 634050, Russia

² Institute of Strength Physics and Materials Science of the SB RAS, Akademicheskoy str. 2/4, Tomsk, 634021, Russia

³ Brunel Centre for Advanced Solidification Technology, Brunel University; Kingston Lane, Uxbridge, UB8 3PH, UK

Composite materials based on aluminum, reinforced non-metallic particles have a high specific strength, hardness, wear resistance, thereby, are of great interest in various fields of science and technology. The most versatile method for their preparation - casting. The template for this composite material, use aluminum alloy A356 system Al-Si, which has good casting and performance, there by providing extensive use in modern engineering.

The main problem for introducing reinforcing particles micro- or nano-particles of oxides, carbides, borides, etc is its uniform distribution in melted metal. One way of solving this problem is ultrasonic treatment of melts leading to grain refinement and dispersion hardening alloy nanoparticles in its structure.

Nanocomposite materials with the matrix of an A356 alloy reinforced with 0.2 and 1 wt% of highelastic nanodiamonds were produced by ultrasonic dispersion of nanoparticles in the melt followed by casting in a metallic mold. The structure as well as the physical and mechanical properties of the cast samples were examined using optical and scanning electron microscopy, hardness and tensile testing. It is shown that the hardness, Young's modulus and electrical resistivity increase with introduction of nanodiamond particles to alloys are much higher as compare with initial state.

Keywords: *Composite material, Aluminum alloy, Nanodiamonds, Ultrasonic treatment, X-ray, Mechanical properties.*

Hydrogen motion in Zircaloy-4 cladding during a LOCA transient

Torres Elodie¹, Desquines Jean¹, Guilbert Severine¹, Baietto Marie-Christine²,
Coret Michel³, Pascal Berger⁴, Blat Martine⁵ and Ambard Antoine⁵
elodie.torres@irsn.fr

¹ Institut de Radioprotection et de Sûreté Nucléaire (IRSN), Centre d'Etudes de Cadarache,
PSN-RES/SEREX/LE2M, BP3, F-13115 Saint-Paul lez Durance Cedex (France)

² INSA de Lyon, Laboratoire de Mécanique des Contacts et des Structures (LaMCoS), UMR 5259,
69621 Villeurbanne cedex, (France)

³ Ecole Centrale de Nantes, Institut de recherche en génie civil et mécanique (GEM), UMR 6183,
44321 Nantes, (France)

⁴ Laboratoire Pierre Sûe, UMR 9956 CEA-CNRS, centre de Saclay, 91191 Gif sur Yvette,
(France)

⁵ EDF-R&D, Les renardières, département MMC, 77818 Moret sur Loing, (France)

Hydrogen and oxygen are key elements influencing the embrittlement of zirconium-based nuclear fuel cladding during the quench phase following a Loss Of Coolant Accident (LOCA). Hydrogen and oxygen follow a complex distribution within the cladding thickness. The understanding of the mechanisms influencing the motion of these two chemical elements is required to fully describe the material embrittlement. We propose in this work to measure oxygen and hydrogen concentrations in clad after a LOCA transient and then compare the results with simulations.

High temperature steam oxidation tests were performed on pre-hydrided Zircaloy-4 samples with hydrogen contents, prior to LOCA transient, ranging between 11 and 400 wppm. Oxidation temperature was 1200°C and durations corresponding to Cathcart-Pawel ECR (Equivalent Clad Reacted) values of 15, 20 and 25% were used. Oxide layer growth, weight gain and hydrogen pick up were measured after high temperature oxidation. The microstructure of the material, especially the phase distributions within the cladding thickness, has been characterized. The radial oxygen concentration profiles and chemical partitioning of the main alloying elements have been quantified by Electron Probe Micro-Analysis (EPMA). The hydrogen distribution and concentration within each phase of the material have been mapped quantitatively using Elastic Recoil Detection Analysis (ERDA). The material embrittlement was finally estimated by post-quenched hoop tensile tests. Image analysis and metallographic examinations were combined to provide an average oxygen profile as well as a hydrogen profile within the cladding thickness after LOCA transient. Surprisingly, the measured hydrogen profile is far from homogeneous. Experimental distributions are compared to calculations derived from the DIFFOX code developed at IRSN.

Keywords: *Zircaloy-4, LOCA, hydrogen, ERDA, diffusion, post-quench embrittlement*

Mechanical Milling of Quasicrystalline Al-Cu-Fe Alloys

P.Yu. Bryantsev, M.E. Samoshina
p_bryant@rambler.ru

National University of Science and Technology "MISiS", 4 Leninskiy prospect, 119049, Moscow,
Russian Federation

The main methods of obtaining quasi-crystalline phases are the creation of the metastable state of metallic materials: rapid crystallization of powders from the melt or mechanical alloying of elementary powders mixture. Formed metastable quasicrystalline phases are sensitive to subsequent treatments (thermal and mechanical). Apart is the method of obtaining the stable quasicrystals by conventional crystallization of massive castings. Stable quasicrystals Al-Cu-Fe can be subjected to high energy treatment in order to grind them up and then use as nano-reinforcers of aluminum composite materials.

Ingots of alloys Al-Cu-Fe were obtained by casting in a graphite mold. Mechanical milling of alloy particles in the cast state and after homogenization annealing was carried out in planetary ball mill Retsch PM400 in an argon atmosphere. As a result of mechanical milling granules with an average size of 35-40 μm and fine internal microstructure are formed. The refinement of phase components was estimated by the change of the size of coherent scattering regions. The size of coherent scattering regions in quasicrystalline phase after mechanical milling was about 10-15 nm. Mechanical milling after homogenization heat treatment allows much refines the quasicrystalline phase than in the case of mechanical milling of cast alloy.

Keywords: *quasicrystals, phase composition, mechanical milling*

Effect of Heat Treatment on Microstructure and Phase Composition of Al-Cu-Fe Alloys with Quasicrystalline Phases

M.E. Samoshina, P.Yu. Bryantsev
samoshina@list.ru

National University of Science and Technology "MISiS", 4 Leninskiy prospect, 119049, Moscow, Russian Federation

Icosahedral quasicrystals Al-Cu-Fe due to unusual internal structure have a number of promising properties: high strength, wear resistance, low coefficient of friction, etc. Therefore, quasicrystals Al-Cu-Fe are considered as a possible material for wear-resistant powder coatings and as a particle reinforcers in dispersion-strengthened composite materials. The main methods of obtaining quasicrystalline phases are the rapid crystallization of powders or mechanical alloying of elementary powders mixture. In this investigation we used the method of obtaining quasicrystals by melting and casting of massive castings in air atmosphere and subsequent heat treatment.

The microstructure and phase composition of alloys Al-Cu-Fe in as-cast state and after heat treatment at different temperatures were investigated. The presence of quasicrystalline phase $Al_{65}Cu_{20}Fe_{15}$ which coexists with different crystalline phases in as-cast condition is found. The formation of single quasicrystalline phase composition in Al - 40 wt.% Cu - 17 wt.% Fe alloy after annealing at 800 °C for 100 hours is established. In alloys Al - 33 wt.% Cu - 22 wt.% Fe, Al - 40 wt.% Cu - 22 wt.% Fe and Al - 33 wt.% Cu - 17 wt.% Fe the single quasicrystalline phase composition is not occur. After heat treatment, i.e. in more equilibrium conditions, the quasicrystalline phase $Al_{65}Cu_{20}Fe_{15}$ is transformed into quasicrystalline phase $Al_{13}Cu_4Fe_3$ with more complicated lattice.

Keywords: *quasicrystals, phase composition, heat treatment, microstructure*

Influence of severe plastic deformation on Portevin – Le Chatelier effect in aluminium 2XXX alloy

Joanna Zdunek¹, Bogusława Adamczyk – Cieslak¹, Jarosław Mizera¹
jzdunek@inmat.pw.edu.pl

¹Materials Science and Engineering Faculty, Warsaw University of Technology, Warsaw 02-507, Poland

The aim of the study was to investigate an influence of a severe plastic deformation realized by different methods on the intensity of the plastic deformation instability (Portevin – Le Chatelier effect – PLC effect) in the commercial 2XXX serie aluminium alloy. To realize the goal extruded aluminium alloy rods were subjected to hydrostatic extrusion (HE), equal channel angular pressing (ECAP) and accumulated plastic strain process (Max Strain). The above methods allow to induce different deformation values from 3.5 to 16 and have a strong influence on microstructure and mechanical properties of the material. The assumption was to refine the microstructure to the nanometric scale. It is known that aluminium alloys very often reveal instability of the plastic deformation which manifests as a serration on the stress – strain curves during the tensile tests. The investigated 2XXX aluminium alloy also exposes this phenomena. It was proved in the experimental works that severe deformation leads to decrease of the instability – especially after equal channel angular pressing the effect has disappeared. The intensity of the Portevin – Le Chatelier effect was describe quantitatively by R_L factor which associates the frequency and the amplitude of the serration on the stress – strain curve. It was assumed that values of R_L factor close to 1 indicates that the deformation in the plastic region is stable and values above 1 are responsible for appearance of the PLC effect. The present work has shown that after ECAP R_L value is 1, after Max Strain 1.2 and after HE 2.1 since the initial state was characterized by R_L value 5.8. This indicates that the deformation path has a significant influence on the intensity of the instability of the plastic deformation PLC in the aluminium 2XXX alloy.

Keywords: *aluminium alloy, plastic deformation instability, severe plastic deformation*

Evolution of microstructure and precipitates in 2xxx aluminium alloy after severe plastic deformation

Bogusława Adamczyk-Cieslak¹, Joanna Zdunek¹, and Jarosław Mizera¹
badamczyk@inmat.pw.edu.pl

¹Materials Science and Engineering Faculty, Warsaw University of Technology, Woloska 141, 02-507 Warsaw

In this paper, the influence of precipitation on the microstructure development in 2xxx aluminium alloy subjected to hydrostatic extrusion was investigated. Three step reduction of the diameter was performed using hydrostatic extrusion (HE) process: from 20mm (initial state) to 10mm, 5mm and 3mm, which corresponds to the logarithmic deformations $\epsilon = 1.4$, $\epsilon = 2.8$ and $\epsilon = 3.8$ respectively. Microstructure and precipitates analysis before and after deformation was performed using a transmission electron microscope (TEM), scanning electron microscopy (SEM) and optical microscopy (OM). As a result of the tests, a very significant influence of precipitation on the degree of refinement and mechanism for transformation of the microstructure was determined.

Keywords: *aluminium alloy, severe plastic deformation, precipitates*

Ultrafine-grain metals by severe plastic deformation for weight lighting

Laszlo S. Toth^{*1,2}, Chengfan Gu^{2,3}

¹laszlo.toth@univ-lorraine.fr, ³chengfan.gu@unsw.edu.au

¹Laboratoire d'Etude des Microstructures et de Mécanique des Matériaux (LEM3),

UMR 7239, CNRS / Université de Lorraine, F-57045 Metz, France

²Laboratory of Excellence on Design of Alloy Metals for low-mAss Structures (DAMAS), Université de Lorraine, France

³School of Materials Science and Engineering, UNSW, Sydney, NSW 2052, Australia

As a relatively simple top-down technique to produce nanomaterials in bulk, severe plastic deformation became a new way of transforming the microstructure of the material. When carried out at sufficiently low temperature, extreme large plastic deformations lead to ultrafine-grain or nearly nano-structured material. The aim of the present lecture is to give basic insight into the field of ultrafine-grain materials obtained by severe plastic deformation. The main features of the obtained microstructures are presented, the most important advantage of ultrafine-grain materials - an enhanced mechanical strength with respect to their coarse grained counterparts - is discussed. The high strength obtained in this way permits to decrease the weight of the metal to bear the same mechanical efforts. The operating deformation mechanisms that lead to the grain refinement are examined. Finally, dynamic recrystallization which produces the ultrafine-grain structure is characterized and the main results of modelling efforts reproducing the grain refinement and several microstructure features are presented

SESSION 9

Membranes and Catalysts

Synthesis of mesoporous titania-10zirconia fibers for CO₂ capture

M.I.Espitia-Cabrera¹, V. Toral-Rangel², M. L. Benjume-Garcia² y M. E. Contreras-García²
iesumich@yahoo.com.mx

¹Facultad de Ingeniería Química Ed. "D", ² Instituto de Investigaciones metalúrgicas, Universidad Michoacán de San Nicolás de Hidalgo Morelia Mich. México

Carbon dioxide (CO₂) released in the atmosphere is the principal cause of the so-called global warming or greenhouse phenomenon. One procedure for the mitigation of CO₂ consists of the capture, transport and geological storage (sequestration) of the gas in porous ceramics. In this study mesoporous titania-10zirconia nanoparticles and NaCl aqueous solution nanofluids to enhance the CO₂ absorption in the base fluid base fluid (NaCl aqueous solution). Samples of titania-zirconia containing 0–10 mol% ZrO₂ composites were synthesized by Sol-Gel, and addition of Tween 20 as template the solution were stirred by two hours, followed by filtration. The gel obtained was used to obtain biomimetic coatings, were coated to hemp fibers. The samples were drying and calcinations at 500 °C during two hours. The coated fibers, were characterized by, BET surface area, X-ray diffraction analysis and scanning electron microscopy

To investigate the crystalline phases, morphological features and surface area of sintered ZrO₂/TiO₂ fiber ceramics after the application of a biomimetic fiber of hemp plant Results obtained were; BET surface area was 90 m²/g, by SEM we observed the surfaces of all TiO₂-10 ZrO₂ fibers were formed with a dense and uniform a globular microstructure. By DRX was observed these fibers are crystalline and the phase obtained was anatase. After the sequestration of CO₂ the results obtained by DRX shows the Na₂CO₃.

Keywords: *titania, zirconia, biomimetic, fiber, storage capacity*

Preparation, Characterisation of $\text{MnO}_x\text{:ZrO}_2$ Sorbents and Application for Mercury Capture

Janos Lakatos¹, and Colin E. Snape²
mtasotak@uni-miskolc.hu

¹University of Miskolc, Institute of Chemistry, Miskolc-Egyetemváros, Hungary, H-3515
²Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, University Park, NG7 2RD, UK

Manganese oxide-zirconia type ($\text{MnO}_x\text{:ZrO}_2$) sorbents were prepared using the sol gel technique by co precipitation $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$. After the solvent evaporation the dried residue was calcinated at different temperature using a tube furnace with a continuous flow of air. The heat treatment below 500 C resulted a high surface area amorphous solid structure (Mn_2O_3 Bixbayit) with and amorphous ZrO_2 phases Fig 1. Using further heating to 1000 C the peletised solid become a hard ceramic network, however it lost the amorphous structure and the high surface area. Fig 2.

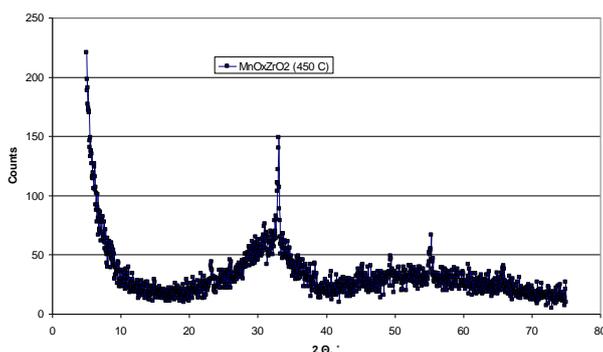


Fig 1. XRD pattern of the ($\text{MnO}_x\text{:ZrO}_2$) sorbents heat treated 450 C

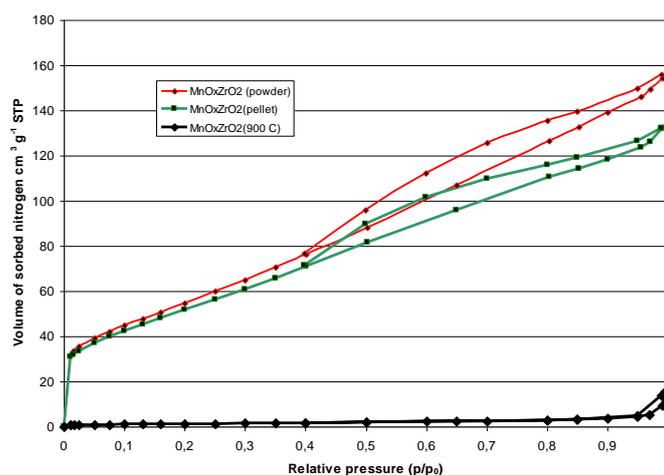


Fig. 2. Nitrogen 77 K sorption isotherms of ($\text{MnO}_x\text{:ZrO}_2$) sorbents heat treated 450 C and structure change after pelletisation and the further heat treatment to build ceramic structure.

The (MnO_x:ZrO₂) sorbents heat treated at 450 C previously found to be efficient for NO_x capture.¹ Using MnO₂ or permanganate for the mercury capture was suggested previously².

The (MnO_x:ZrO₂) sorbents heat treated at 450 C was found high efficient for mercury capture from gas stream Table 1. The mercury sorption tests have indicated that the equilibrium capacity of this adsorbent is close to 30 % w/w which corresponds to an atomic Mn:Hg ratio close to 1:1. These sorbents are much more effective than the precipitated manganese-oxide and the zirconia support and the other carbon base sorbents available on the market³.

Table 1. Comparison of BET surface area and Hg sorption capacity of the produced sorbents

Sorbent	BET surface area, m ² /g	Dilution ratio (Sorbent/sand by volume)	Breakthrough capacity, % w/w Hg
ZrO ₂ (75~250 μm)	127	1:0	<0.002
MnO _x /ZrO ₂ (75~250 μm)	228	1:3	17.5
MnO _x /ZrO ₂ (75~250 μm)	228	1:0	22.6
MnO _x (75~250 μm)	11	1:1	2.0

References

1. Eguchi, K.; Hayashi, T. Reversible sorption-desorption of NO_x by mixed oxides under various atmospheres. *Catalyst Today* 1998, 45, 109-115.
2. Janssen, J. H.; Van den Enk, J. E.; Bult, R.; De Grott, D. C. Determination of total mercury in air by atomic absorption spectrometry after collection on manganese dioxide. *Anal. Chim. Acta*, 1977, 92, 71-77.
3. Snape, C.E., Sun C., Lakatos J., Perry R.: Sorbent Composition WO patent: WO 2008/093137 A1. Publ. date: 7 Aug. 2008.

Changeing of Fly Ash Leachability after Grinding

Janos Lakatos¹, Roland Szabó², Adam Racz², Oliver Banhidi¹ and Gabor Mucsi²
mtasotak@uni-miskolc.hu

¹Institute of Chemistry, Faculty of Material Science and Engineering, University of Miskolc,
Miskolc-Egyetemváros, H-3515, Hungary

²Institute of Raw Materials Preparation and Environmental Processing, Faculty of Earth Science and
Engineering, University of Miskolc, Miskolc-Egyetemváros, H-3515, Hungary

The aim of this study was to follow the mineral transformations of fly ash used for geopolymer production during mechanical activation. There are different direct instrumental methods TG, IR, XRD, NMR, XPS, etc. which are able to detect the change of the surface and the crystal structure, however the sequential extraction based on the solubility change can provide direct information about the alteration of the structural element mobility after the treatment. Beside the demonstration of the structural change the extraction can provide valuable information for the potential of tested raw in geopolymer production. Mechanical activation of lignite fly ash was carried out by a conventional tumbling ball mill under dry condition. Different activation times between 0-60 min were used. The solubility tests were carried out by distilled water, H₂O, weak acid (1 M acetic acid, HAc) and strong acid (2 M nitric acid, HNO₃) and by different concentration alkaline solutions, (1-10 M NaOH). 1:50 solid liquid ratio and 14 days contact time in static condition were used. The sequential extraction test of solids is generally used for determination of the environmental risk if the waste is intended to be disposed to the environment. Rarely this technique is used in hydrometallurgy to find the suitable process for extraction of the valuable component (e.g. planning the suitable recycling technologies). This work intends to demonstrate that it can be a sensitive technique for following the structural change during the mechanochemical treatment of solids.

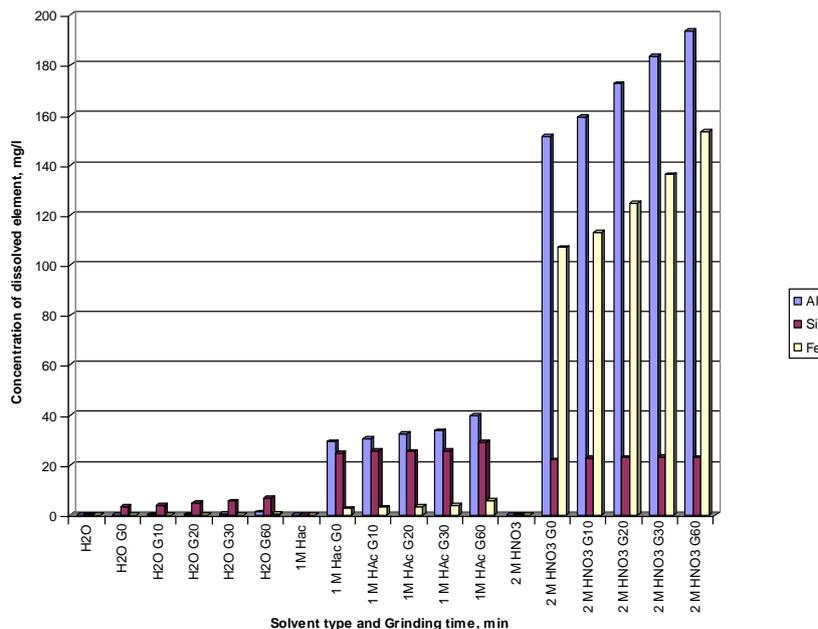


Fig.1 Demonstration of changing of Si, Al, and Fe solubility of fly ash in function of grinding.

Fig. 1 shows, how the mobility of the main elements: Si, Al, Fe of the fly ash has changed in function of grinding time. The improvement of solubility in function of grinding time is well visible. Similar conclusion can be done from the extraction tests conducted by alkaline solutions, see Table 1.

Table 1. Effect of grinding on the alkaline soluble components of fly ash(G0-G60) and micronised silica powder(MS)

1 M NaOH			
Concentration of dissolved elements, mg/g			
t(grinding), min	Si	Al	Fe
G 0	1,8	0,76	0,72
G 5	1,7	0,73	4,54
G10	2,1	1,00	2,35
G20	2,5	1,53	1,74
G30	2,3	1,44	1,67
G60	3,1	2,04	0,63
MS	66,1	0,74	1,10
5 M NaOH			
Concentration of dissolved elements, mg/g			
t(grinding), min	Si	Al	Fe
G 0	10,4	4,91	0,34
G 5	11,2	5,28	0,39
G10	11,7	5,66	0,37
G20	13,6	6,50	0,38
G30	13,2	6,23	0,32
G60	17,2	7,21	0,38
MS	153,2	2,07	0,26
10 M NaOH			
Concentration of dissolved elements, mg/g			
t(grinding), min	Si	Al	Fe
G 0	7,7	4,59	0,75
G 5	8,7	6,15	1,58
G10	7,8	5,45	0,86
G20	9,5	6,18	0,85
G30	16,4	9,77	0,45
G60	14,3	8,49	0,97
MS	6240	0,86	0,2

Both tests have proved that the grinding can provide such kind of structural changes which resulted higher solubility for the elements of fly ash which play crucial role in network formation if the fly ash used for geopolymer production.

Acknowledgements

The research work was performed primary in the framework of TET Indo-Hungarian collaboration project(Geopol 10) and project GOP-1.1.1-11-2012-0379.

Planar Photonic Crystal Nanocavities Incorporating Hybrid Silicon/Polymer Material for All-Optical Switching

L Kassa-Baghdouche^{1,2}, T Bouchemat¹, M Bouchemat¹, E Cassan³
kassabaghdouche_lazhar@yahoo.com

¹ Laboratoire Microsystèmes et Instrumentation (LMI), Université Constantine 1, Constantine, Algérie

² Faculté des Sciences et de la Technologie, Université 8 mai 1945, Guelma, Algérie.

³ Institut d'Electronique Fondamentale, Université Paris-Sud, Orsay 91405, France

We present a novel design and analysis of two-dimensional planar photonic crystal nanocavities in thin silicon membranes well suited for all-optical switching. The cavity geometry is based on Si photonic crystal membrane sandwich between two optically thick cladding layers. Our concept cavity is made from infiltrating the air hole array and coating the surface of usual photonic crystal membrane with polymer. In view of practical realization of this hybrid structure, it is necessary to investigate the dependence of the optical properties of nanocavity on the refractive index of surface cladding. We show that when the refractive index of the cladding is increased from 1 to 1.53, corresponding to that of organic polymers, the Q-factor markedly decreases. We then discuss the design of high-Q nanocavity after which the polymer is introduced into the air void to form the hybrid structures. Optimization of the cavity design by modulating the structure parameter yields a high quality factor with a small modal volume across the telecommunications band. In addition the field distribution of the resonant mode indicates that the radiation loss is sufficiently small. Due to the overwhelmingly large Kerr nonlinearity of polymer over silicon, this hybrid silicon-polymer nanocavity configuration show great promise to realize very fast response speed and low pump intensity in small sized all-optical switching devices or circuits and allow for easy integration with other integrated optical components.

Keywords: *Planar photonic crystal, L3 nanocavity, 3D-FDTD, Photonic integrated circuits.*

Formation of Catalyst Model Dispersed for the system Pd/MgO (100)

F.Baara¹, A.Chemam²
a.chemam@epst-annaba.dz

Laboratory of surfaces and interfaces of solids studies - (LESIMS) –

¹*Department of Physics, Faculty of Sciences, Badji Mokhtar University-Annaba-Algeria.
baarafatma@yahoo.fr*

²*Preparatory School for Science and Technology of Annaba, ,Annaba 23000, Algeria
Corresponding author:*

We performed calculations and recounts of various parameters related to the first quantitative study on the nucleation and growth of a catalyst model dispersed Pd /thin MgO (100) which was deposited at substrate temperatures ranging from 573K- 1073K. This simulation was performed by developing a new programs using Fortran. The nucleation kinetics are interpreted according to the theory of random nucleation, it follows that the general scheme is consisting of three stages: nucleation, growth and coalescence. It is shown that the saturation density of clusters decreases when the substrate temperature increases in following Arrhenius law. This behavior is in agreement with a recent AFM study for Ag/MgO and Au/MgO. The phenomena of coalescence can be explained by the process of island migration. The coalescence occurs at high substrate temperature more rapidly than at lower substrate temperature.

Keywords: *Model Catalyst, Palladium, Nucleation, Growth and Coalescence.*

High temperature stable non-oxide ceramic membranes for gas separation

Yvonne Jüttke¹, Hannes Richter¹, Ingolf Voigt², Michael Stelter³
Yvonne.juettke@ikts.fraunhofer.de

¹Department of Nanoporous Membranes, Fraunhofer Institute for Ceramic Technologies and Systems, Hermsdorf, Thuringia, Germany

²Deputy Institute Director, Fraunhofer Institute for Ceramic Technologies and Systems, Hermsdorf, Thuringia, Germany

³Technical Environmental Chemistry, Friedrich Schiller University Jena, Jena, Thuringia, Germany

Adsorption, absorption as well as cryogenic distillation are established processes for gas separation. Membrane separation is gaining more and more interest because of its higher energy efficiency. Polymer membranes are available but their application is limited to low temperature. Therefore it's essential to expedite the development of high temperature stable inorganic membranes. Zeolites, amorphous oxides, carbon, ionic conducting ceramics as well as novel metals have already been used for membrane preparation. The performance of these membranes has been demonstrated successfully in lab and pilot scale up to 400 °C. Non-oxide ceramics like silicon carbonitride (SiCN) and silicon carbide (SiC) are well known for much higher stability up to 1000 °C.

SiC and SiCN membranes were prepared as thin nanoporous layers on top of mesoporous ceramic substrates (γ -Al₂O₃ and ZrO₂ substrates on pure alumina supports) with a polymer containing silicon, carbon (and nitrogen) in a solution followed by crosslinking reactions and pyrolysis above 600 °C in inert gas atmosphere. The final membranes were characterized via permeometry and FESEM/EDX measurements.

High permselectivities were achieved in single gas permeation measurements at 300 °C. SiCN membrane shows nearly a hundred twenty times higher permeances of hydrogen to propane. The Knudsen selectivity for this gas mixture averages only at 4.7. Unfortunately, the SiCN membranes showed no molecular sieving behavior for the separation of H₂/CO₂ mixtures. With SiC membranes excellent results for the H₂/C₃H₈ separation and even for H₂/CO₂ mixtures in real media could be achieved.

Therefore, membranes with high molecular sieving content were successfully prepared. Shape-selective molecular sieving allows separation of compounds based on size and geometry. This mechanism requires the pore size of the membrane to be in between the molecular diameters of the compounds of a gas mixture. In the case of molecular sieving selectivity and permeances are most widely independent from pressure and temperature.

Keywords: PDC, nanoporous membranes, gas permeances, permeometry, SiC(O), SiCN(O)

SESSION 10

Minerals for Environmental and Medical Application

Physical and crystallographic properties of aluminum minerals and red mud

Olga Kotova, Valery Silaev, Vladimir Lutoev, Alexander Vakhrushev
kotova@geo.komisc.ru

Laboratory of Mineral Raw Technology, Institute of Geology Komi SC UB RAS, 167982 Syktyvkar,
Russia

Physical and crystallographic properties of aluminum minerals and red mud and ways of their modifying for expansion of their application in industry are presented. Bauxites are main, technological and economic raw material for production of alumina and aluminum. The main part (85%) of alumina is consumed by aluminum industry, the rest is used for production of various technical materials, such as heat resisting and acid resisting refractory, electrocorundum, extra strong aluminous cement, corundum ceramics, various composites, etc.

Bauxites are complex, thin- and ultradisperse ores by valuable components. A considerable "diffusion" of mineral concentration reduces economic expediency of their development by existing ways and demands new technological decisions. The results of mineralogical-crystallochemical researches of bauxite minerals and red mud by high-resolution electronic microscopy, chemical and thermal analyses, X-ray diffraction, IR- and Moessbauer spectroscopy are presented.

Low ferriferous bauxites (iron content in Fe_2O_3 is less than 4% for ignited substance) – raw material for technical materials (corundum ceramics, coagulants – aluminum salts for sewage treatment). Semiconductor properties of ceramics depending on modes of production are studied. The ion-exchange feature aluminum salts for production of coagulants is studied.

The firebrick well conducts heat, resists the influence of chemicals, stands $T = 1600$ °C. It is used in metallurgical and glass production, for building of factory furnaces, fireplaces, porcelain roasting, etc. Bauxite processing into alumina results in the formation of significant volume of wastes – red mud (RM), which is taken off from the process as pulp and drained to slime storages, increasing the costs of the main production of plants. New technologies of waste-free processing of raw are discussed, which would allow to increase alumina extraction, to obtain iron- and titanium-rich RM and create new materials for environmental application.

Keywords: aluminum minerals, red mud, modification properties, new materials

Physics and chemistry of minerals under laser processing

Olga Kotova¹, Nina Leonenko²
kotova@geo.komisc.ru

¹Laboratory of Mineral Raw Technology, Institute of Geology Komi SC UB RAS, 167982 Syktyvkar, Russia

²Institute of Mining FEB RAS, 680000 Khabarovsk, Russia

Lasers are used in processing technologies of separate types of mineral raw (for example, for uranium enrichment). Wide introduction of this direction has a very slow progress. Principal causes are insufficient study of mechanisms of laser influence on mineral substance and low level of laser technologies for processing and enrichment, which results in problems of transition from laboratory researches to industrial production.

The process of interaction of laser irradiation with mineral substance is characterized by a number of important features in comparison, for example, to mechanical influence. The degree of influence of laser irradiation on mineral (ore) depends only on the ability of the latter to absorb the irradiation of the given laser wave length, while the mechanical processing is based on such features as hardness and viscosity of the processed material. Power consumption during hyperfine mechanical crushing exceeds 80 kWh/t. Laser processing of fine mineral raw allows overcoming physical resistance of ores without excessive overmilling; the material is redistributed with agglomeration of useful minerals and formation of new phases. At that power consumption is comparable for extraction of fine and sublimated valuable minerals, but a higher degree of influence selectivity is reached.

Object of researches - natural magnetite from gold placers and bauxites. Modern analytical methods were used for process control in the mineral–laser irradiation system.

Physical and chemical properties of fine and sublimated valuable minerals, first of all: melting temperature, reactivity, electric conductivity, magnetization, hardness, are considerably different from macroindividuals and even microindividuals due to larger part of surface atoms.

Under the influence of laser irradiation the concentration and agglomeration of both heavy metals, and precious metals, occur, in particular: gold - into larger structures with greater chemical purity in comparison to initial mineral associations. Such researches can become a scientific basis for the development of new extraction technologies of submicronic gold, titanium and other valuable minerals and for creation of new materials.

Keywords: magnetite, bauxite, laser processing, modification properties, new materials

Titanium minerals for new materials

Olga Kotova¹, Elena Ozhogina², Alexey Ponaryadov¹, Irina Golubeva¹
alex401@rambler.ru

¹Laboratory of Mineral Raw Technology, Institute of Geology Komi SC UB RAS, 167982 Syktyvkar, Russia

²Mineral department, All-russian scientific-research institute of mineral resources, 119017 Moscow, Russia

Comparative study of titanium minerals of modern coastal-marine placer on North Stradbroke Island (East Australia) and Pizhemsкая paleoplacer in Middle Timan (Russia) has been carried out by modern mineralogical and analytical methods. These placers have one of the world's largest reserves of titanium ore (TiO_2 , FeTiO_2 , Fe_2TiO_3). Both placers are polymineral. Mineral sands and silica sands are main product streams of industrial production. The minerals extracted are used in glass, digital tablets (iPads), metals, plastics, paints, photocatalyst, ceramics production, in medical and food industries, etc. Ilmenite are prevalent in the heavy sands of Stradbroke. Leucoxene are generally far more prevalent in mineral sand ore bodies of Pizhemsкое placer in comparison with Ilmenite and rutile. Pizhemsкая ore has the isomorphic impurity, independent mineral phases of the titan and other metals and more problems to dress.

Physical properties of titanium minerals (magnetic, electrical, sorption, etc.) were studied. Ilmenite has a high magnetic susceptibility and electrical conductivity compared with zircon and rutile – low magnetic susceptibility and a high value of electrical conductivity. Various methods of modification of physical and chemical properties are used to increase contrast of ores and host rocks. One of a way to change magnetic properties of minerals is γ -radiation. Modification of mineral properties increases the list of products of the industry. New methods to change mineral properties and to create new materials are discussed.

The work was done under financial support of RAS programmes (projects 14-5-IP-52 and 12-T-5-1022).

Keywords: heavy sands, titanium minerals, properties modification, new materials

Antibacterial activity of Vanishing Creams incorporated with ZnO nanoparticles against *Propionibacterium acnes*

Roselin Polugari¹, Shailaja Raj Marla¹
roselinpolugari@gmail.com

¹Department of Microbiology, St. Francis College for Women, Hyderabad, India

Research related to the antibacterial activity of nanoparticles will enable new developments in the field of Nano medicine. *Propionibacterium acnes*, a gram positive, non-motile, nonsporulating and microaerophilic bacillus causing acne. The treatment for acne using Benzoyl peroxide and tetracycline though effective, has side effects hence there is a need to find a novel and appropriate method to treat acne. *P. acnes* was isolated from different individuals suffering with acne and was identified by using various biochemical characters, FAME analysis and 16s r RNA typing. Bulk ZnO is used in baby powders and creams to treat diaper rashes because of the mild activity of Zn on skin. Based on these reports, the present study focused on the use of ZnO nanoparticles in treating acne. The ZnO nanoparticles were synthesized using different chemical methods and a comparative study of the antibacterial activity of the nanoparticles against *P. acnes* was demonstrated by using Agar well diffusion method and the size of the Zone of Inhibition was measured. The nanoparticle which showed very good activity and stability was characterized using XRD, TEM, SEM, TGA, FTIR and WD spectroscopy. The nanoparticles were then incorporated into different creams and the antibacterial activity of the cream and the stability of the nanoparticles in the cream were analyzed. Tissue culture and Animal studies were carried out to demonstrate that the ZnO nanoparticles were specific in their activity against *P. acnes* and nontoxic to the host cells. The present study concludes that a novel way of treating acne would be the topical application of Vanishing cream incorporated with ZnO nanoparticles.

Keywords: ZnO nanoparticles, *Propionibacterium acnes*, Acne, Antibacterial activity, Vanishing creams

Role of Microorganisms and Magnetite Nanoparticles in Metal Adsorption released from E-waste

Gayatri.Y, Shailaja Raj .M
shailarm@yahoo.com

Department of Microbiology , St.Francis College for Women, Hyderabad, India

Electronic Waste or E-waste is the term used to describe products such as computers, laptops, TVs, DVD players, mobile phones, mp3 players etc. which have been disposed into the environment. Electrical and electronic equipment are made up of a multitude of components, some containing toxic substances. If these are left untreated and disposed in landfills or not recycled by using proper methods of recycling, they leach into the surrounding atmosphere, soil and water and cause adverse effects on human health and environment. Many elements of this waste contain poisonous substances such as lead, tin, mercury, cadmium and barium, which cause severe diseases like cancer, birth defects, neurological and respiratory disorders. Informal processing of electronic waste in developing countries causes serious health and pollution problems.

The present study focuses on metal adsorption studies by microorganisms isolated from E-waste soil dumping yards and magnetite nanoparticles. Microorganisms were collected from four different areas such as Maheshwaram, Shameerpet, Musheerabad and Jawaharnagar dumping yards in and around Hyderabad, India. Gram positive bacilli and cocci were isolated and identified by biochemical methods. Since Iron-based magnetic nanomaterials (Magnetite) have unique properties, such as larger surface area-volume ratio, diminished consumption of chemicals, and no secondary pollutant were synthesized by co-precipitation process and further used for adsorption studies. Magnetite nanoparticles were characterized by XRD and the size was determined to be 99nm. Lead an important component of many electronic goods was undertaken for adsorption studies by bacteria isolated from E-waste soil and magnetite nanoparticles using Atomic adsorption spectrophotometer. Effect of different metal concentrations ranging from 5ppm to 20ppm was analyzed. It was observed that metal adsorption by magnetite nanoparticles was more at 15ppm concentration which is 162.83mg/L and by bacteria greater adsorption was observed at 5ppm which is 151.89mg/L where the initial metal concentration is 173.95mg/L . Contact time studies also emphasized greater adsorption at 30min, 4h and 24h by both magnetite nanoparticles and bacteria. Metal adsorption was higher by magnetite nanoparticles when compared to bacteria isolated from E-waste soil.

Hence the present study is proposed to explore bacteria for the determination of their tolerance capacity in and around the areas of Hyderabad where heavy metal ions are leached and also to prepare microbial iron nanocomposites which can act as potential geoactive agents.

Keywords: *E-Waste , Magnetite nanoparticles ,Heavy metals , Adsorption studies*

Magnetic properties of natural titanium minerals

Yury Ryabkov¹, Olga Kotova², Irina Piir¹, Svetlana Rubtsova¹,
Nikolay Sekushin¹, Ekaterina Tsvetkova¹
ryabkov-yi@chemi.komisc.ru

¹Laboratory of Ceramic Materials, Institute of Chemistry Komi SC UB RAS, 167982 Syktyvkar, Russia

²Laboratory of Mineral Raw Technology, Institute of Geology Komi SC UB RAS, 167982 Syktyvkar, Russia

Ilmenite is natural iron titanate FeTiO_3 , and ilmenite rocks are an important raw source for the production of titanium, pigments, magnetic, electrical and photoactive materials. On the other hand ilmenite transition elements titanates have a unique set of magnetic and electrical properties. Detailed studies of the Moon and Earth ilmenites are important for explaining the magnetism of our planet and its natural satellite.

Feature of the magnetic sublattice structure of ilmenites MTiO_3 is the alternation of non-magnetic and magnetic atoms - titanium (IV) and transition metal (II) oxygen octahedra layers. Such laminar magnetic structure causes a variety of properties of minerals and their synthetic analogues.

The MTiO_3 ilmenite structure distortions arise due to the isomorphous substitution of atoms in M-position. The heterovalent substitution is possible up to 10 atomic % without destroying the structure. Ratio of Fe (III) / Fe (II) determines the total changing in ilmenite FeTiO_3 . The lattices doping by the nonmagnetic atoms is widely used for creating of new materials with desired electrical properties.

We have identified various ilmenite changes and synthesized ilmenite solid solutions in the system $\text{M}^i\text{TiO}_3 - \text{M}^{ii}\text{TiO}_3 - \text{M}^{iii}\text{TiO}_3$ ($\text{M}^i, \text{M}^{ii}, \text{M}^{iii} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Mg}$). On the basis of X-ray and magnetic studies it was shown the ability of ilmenite structure to stabilize the divalent state of the atoms in the M-sublattice at low concentrations. For the dilute solid solutions of iron it explains the low magnetization and absence of ferromagnetic exchange interactions that occur in natural ilmenite rocks due to the formation of solid solutions of ilmenite- hematite.

Purposeful formation of atomic (magnetic) sublattices is focused on the development of new ilmenite materials with desired physical properties.

Work is supported by the fundamental research program of UB RAS (project №12-35-M-2055) and RFBR (project № 13-03-00132).

Selenium, tellurium and precious metal mineralogy in Uchalinsk copper-zinc-pyritic district, the Urals

Ilya Vikentyev
viken@igem.ru

Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Rus. Acad. Sci.,
119017 Moscow, Russia

The Uchalinsk is the second copper-zinc-pyritic district of the Urals with > 400Kt of massive sulfide ore and >16Kt of Cu+Zn. During processing the most of Au, Ag, Pb, Se, Te, Bi, Sb, As, Hg as well as notable part of Cu, Zn and Cd fall for tailings and became heavy metal pollutants. The study of mode of occurrence of Au, Ag, Te and Se covers two giant VHMS deposits: Uchaly (intensively deformed) and Uzelginsk (altered by late hydrothermal processes) as well as middle-sized Molodezn and West Ozern deposits (nondeformed). Specific feature of these deposits of D_{2e1} age are Zn > Cu and uplifted levels of Te, Se, As, Au and Ag in ores of the deposits. Proper minerals of compounds with Te, Au and Ag routinely form fine inclusions inside of common sulphides of the ores: sphalerite, chalcopyrite and pyrite. Gold was mostly concentrated in pyrite and chalcopyrite (1 - 20 ppm) in the mode of "invisible" gold; silver occurred mainly as isomorphic component of tennantite-tetrahedrite series (0.1-6 wt % Ag). Au-bearing mineral parageneses of VMS deposits (including native gold, other native elements, tellurides, fahlore, enargite) were formed on the latest stage of mineralisation. Late hydrothermal stages and local metamorphism of sulphide ores resulted in redistribution of non-ferrous and precious metals: refining of common sulphides, segregation of rare elements and appearance of submicron isolations of Au-Ag alloys (fineness 451-882), Au and Ag compounds with Te, Se, Bi, As, Sb, S. A lot of tellurides (altaite, hessite, stützite, petzite, empressite, coloradoite, tellurobismuthite etc.) as well as and native elements (Au-Ag, Ag, Te, Re) occur in massive sulphide ores. Au-Ag alloys are relatively common and sulphides (argentite, petrovskaitite, uyttenbogaardtite), sulphotellurides (tetradymite) and sulphoarsenides (pearceite, pearceite-polybasite) are rare. Minerals of Se (unreported for Urals previously): kawazulite-tetradymite $\text{Bi}_2\text{Te}_{1.9}(\text{Se}_{0.57-0.65}\text{S}_{0.3-0.26})$, clausthalite and Pb_2SeS . Some minerals contain Se as admixture: galena (up to 0.45 wt%), pyrite (up to 511 ppm), sphalerite (up to 471 ppm), chalcopyrite (up to 313 ppm), pyrrhotite (up to 363 ppm) and etc.

Keywords: *minerals, selenium, tellurium, silver, gold, massive sulfide, copper-zinc-pyritic ore, pollutants, Urals*

Occurrence Modes of As, Sb, Te, Bi, Ag in Sulfide Assemblages of Gold Deposits of the Urals

Olga Vikentyev, Ilya Vikentyev
ovikenteva@rambler.ru

Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Rus. Acad. Sci.,
119017 Moscow, Russia

The Urals is the oldest (266 years) gold-mine province of Russia. About 60 million tonnes of sulfide-related gold processing (gravity separation and flotation) tailings waste are stored all over the Urals. Approximately the same is quantity of pyrite-bearing (1-5 vol%) overburden and ore stockpiles excavated during mining. Arsenic, antimony, copper, zinc, lead, tellurium, cadmium, mercury containing in pyrite are "potentially pollutants". These rare elements of ores as well as gold and silver are in the focus of the study covering Berezovsk, Svetlinsk and Vorontsovsk large gold deposits. Microprobe analyses of gold-bearing sulfides were carried out using an electron-probe microanalyser (EPMA). The contents of chemical elements in minerals were examined by instrumental neutron activation analysis (INAA) for bulk samples and mineral concentrates (50 mg). First laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS, LabMaTer at the Université du Québec à Chicoutimi) data have been obtained for pyrites from the Svetlinsk and Vorontsovsk deposits. Dominant opaque minerals routinely filling the fractures in quartz and impregnated in host rocks is pyrite; tennantite-tetrahedrite, sphalerite, galena and chalcopyrite are less common; for Vorontsovsk deposit arsenopyrite is usual. The sulfide contents range from 2 to 10 vol%. Major Au mineral is native gold bearing 70-100 wt % of its total balance. Sulfides contain a lot of impurity elements: pyrite bears As 38 ppm-8.5 wt%, Sb <1 ppm-3.8 wt%, Se <1-131 ppm, Hg 0.1-108 ppm and Ag <0.2-104 ppm; sphalerite contains Cd 0.14-0.89 wt%; As 3 ppm-0.20 wt%, Sb 1-63 ppm, Hg 13-45 ppm and Ag 6-57 ppm; chalcopyrite Ag 0.07-0.18 wt%, galena As up to 1986 ppm, Sb up to 811, Bi 0.3-3.1 wt%, Ag 0.1-2.51 ppm; tennantite Bi up to 3.6 wt%, Hg 0.02-0.13 wt%; arsenopyrite Ag <1-185 ppm. These elements as well as silver occur mainly as isomorphic component of sulfides and sulfosalts. Proper minerals are common for As+Sb (tennantite-tetrahedrite), Bi and Te (tellurides, sulfotellurides).

Keywords: *minerals, arsenic, antimony, tellurium, mercury, silver, gold ore, pyrite, potentially pollutants, Urals*

Wet grinding of zeolite in stirred media mill

Gábor Mucsi¹, Katalin Bohacs¹,
ejtbohacs@uni-miskolc.hu

¹Institute of Raw Material Preparation and Environmental Processing, University of Miskolc, 3515 Miskolc, Hungary

Zeolites have well-defined crystalline structures with nanopores that are in the molecular size range, are ion exchangeable, and show high chemical and hydrothermal stability. Zeolite nanocrystals are believed to have advantages, over zeolite microparticles, in that they have larger external surface areas and shorter diffusion path lengths. The improved properties of the zeolite nanocrystals could possibly lead to promising applications related to catalysis, diffusion, adsorption, ion exchange, etc... Controlling the size of zeolite crystals is essential for making effective use of these materials in many existing and potential applications.

In the present study, systematic experiment series were carried out in order to produce zeolite nanoparticles from microparticles using a wet stirred media mill. The aim of research was to optimize the experimental conditions of wet stirred media milling which could lead significant reduction in the particle size with minimal loss in crystallinity. The diameter of the grinding media as well as the rotor velocity and residence time were varied in the experiments. Particle size distribution of the ground samples were measured by laser particle sizer to determine the variations occurring in the particle size and „outer” specific surface area when wet stirred media mill was applied. Additionally, XRD, FT-IR and BET analyses were performed for the characterization of the crystalline and material structure, as well as the „total” specific surface area respectively.

Based on the results of the laboratory experiments it was found that wet stirred media milling provided significant reductions in the particle size of zeolite. Furthermore, crystalline structure defects were observed when relatively long milling times were employed.

Keywords: *nanogrinding, wet stirred media mill, zeolite*

TiO₂ dispersions in waters and sediments of the Frido River, Italy: Environmental risk assessment

Antonio Lettino, Claudia Belviso, Francesco Cavalcante, Saverio Fiore
saverio.fiore@cnr.it

Institute of Methodologies for Environmental Analysis, CNR, Tito Scalo, Potenza – Italy

Titanium dioxide exists in nature in three different crystalline forms: rutile, anatase and brookite. Rutile and anatase are the most common phases; they are accessory minerals in different types of igneous and metamorphic rocks also found as mineral grains in the clastic sedimentary rocks. Some literature data showed that nanosize TiO₂ particles may represent potentially harmful risks to human health and indicated oxidative stress as the main toxicity mechanism. It has documented that toxicity of TiO₂ particles mainly depend on physical and mineralogical characteristics of the particles., i.e., size, specific surface and crystalline form.

Although the main documented risk is usually associated with the anthropogenic TiO₂ dispersion, in this work an area characterized by large outcrops of ultramafic rocks were investigated to evaluate the mineralogical risk due to TiO₂ dispersion. Samples of rocks, sediments and surface water were collected to determine physicochemical and mineralogical factors indicative of the TiO₂ potential toxicity.

X-ray diffraction data showed the presence of titanium oxides as rutile and anatase crystalline. SEM (scanning electron microscopy) images displayed nano-to-micro TiO₂ phases with fibrous morphology observed either isolated or enclosed in phyllosilicates.

The results indicate that mineralogical risk due to environmental dispersion of titanium dioxide in nature is possible. This risk is correlated not only with the TiO₂ presence in the source rocks but also with their presence in rocks degradation products (eluviali, fluvial and colluvial detritus). These products represents, in fact, important secondary sources of mineralogical risk, sometimes located quite distant from source rocks due to the action of surface water which, in addition to being a carrier of TiO₂ in the environment, may themselves be sources of risk.

SESSION 11

Nanomaterials for Environment and Health

Morphological Controlled Synthesis and Oxygen Storage Capacity of SnO₂

Mizuki Yoshida, Qiang Dong, Shu Yin and Tsugio Sato
miduki@mail.tagen.tohoku.ac.jp

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

Ceria (CeO₂) and CeO₂-based mixed oxide possessing oxygen storage capacity (OSC) have been used as the co-catalysts for automobile exhaust-control three way catalysts. Recently, it has highly desired to improve the performance of three-way catalyst for environmental cleanup, as well as reducing the use of Ce, since Ce is one of the expensive minor metals. SnO₂ is one of the candidate materials for novel OSC materials, since the valence of SnO₂ can change from 4+ to 2+ reversibly, while that of CeO₂ changes from 4+ to 3+. In addition, it is easy to control the morphology of SnO₂ particles by a variety of synthesis methods, and the OSC of SnO₂ may be improved by controlling the morphology and chemical modification.

In the present study, various morphologies of SnO₂ particles were synthesized by solvothermal method as follows, and the effect of alkali earth metal ion doping on the thermal stability and OSC of SnO₂ was evaluated. The porous SnO₂ particles were prepared by evaporating SnCl₂ ethanol aqueous solution using spherical SiO₂ nanoparticles as the template, followed by the dissolution of SiO₂ particles with NaOH aqueous solution and calcination at 350°C for 5 h. The aggregates of SnO₂ nanoparticles were prepared by the hydrothermal reaction of SnCl₂, sodium citrate and NaOH ethanol aqueous solution at 180°C for 12 h, followed by calcination at 400°C for 2 h. The hollow structured SnO₂ particles were prepared by the hydrothermal reaction of SnCl₄ ethanol aqueous solution at 180°C for 24 h using D-glucose as a template. All samples were annealed at 1000°C for 20 h to evaluate the thermal stability

All samples consisted of single phase of rutile structure. The specific surface areas of the aggregates of SnO₂ nanoparticles and hollow structured SnO₂ particles decreased to 13.5 and 8.3 m²/g, respectively, after calcination at 1000°C, but the porous SnO₂ particles retained relatively larger specific surface area of 21.6 m²/g, indicating the excellent thermal stability. The OSC of the samples changed depending on the specific surface area in the order porous SnO₂ particles > aggregates of SnO₂ nanoparticles > hollow structured SnO₂ particles, where the porous SnO₂ particles showed the OSC superior to CeO₂. The thermal stability and OSC of porous SnO₂ particles could be greatly improved by doping with alkali earth metal ions such as Sr²⁺ and Ba²⁺, but degraded by doping with Ca²⁺ and Mg²⁺.

Keywords: SnO₂, oxygen storage capacity (OSC), morphology

Synthesis and Their Gas Sensing Properties of Different Morphologies of SnO₂

Makoto Hamanaka¹, Shu Yin¹, Qiang Dong¹, and Tsugio Sato¹
hamanaka@mail.tagen.tohoku.ac.jp

¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
2-1-1, Katahira, Aoba-ku, Sendai 980-8557, Japan

Metal-oxide semiconductor gas sensors have been attracted attention in the point of view of personal safety, medical diagnosis, detection of pollutants and toxins and the transportation industries. Among metal-oxides, tin dioxide (SnO₂), a well know n-type wide band gap semiconductor ($E_g = 3.6$ eV, at 300 K), is considered as one of the most promising functional gas sensing materials due to its high gas sensitivity, high stability and low cost. Gas sensing properties of SnO₂ depend on its morphology such as quantum dots, nanowires, nanorods, nanosheets and so on. Moreover, loading of additives such as metals and metal oxides promotes the gas sensitivity of the oxide semiconductor gas sensor. However, the gas sensing properties of various morphologies of SnO₂ nanomaterials have not been systematically investigated.

In this study, four different morphologies of SnO₂ (nanorods, nanosheets, nanoparticles and nanodots with the specific surface area of 2.7, 6.2, 16.5 and 156.7 m²/g, respectively) were synthesized by liquid-phase methods. In addition, Pt was loaded on each prepared SnO₂ by UV light irradiation after dispersing SnO₂ particles and PtCl₄²⁻ in methanol aqueous solutions. The resultant products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) theory. The gas sensing properties of synthesized SnO₂ were tested by detecting the change in the electric resistivity in the presence of acetone and methanol gases.

Gas sensing properties greatly changed depending on not only specific surface area, but also exposed crystal plane, i.e., SnO₂ nanorods showed excellent sensitivity and quick responsivity, indicating the excellent gas sensing ability of the (111) plane. Furthermore, the Pt loading enhanced the gas sensing properties of SnO₂ exceedingly.

Keywords: SnO₂, Gas sensor, Morphology, Pt loading

Environmentally friendly composites for construction in the Arctic region

Prof Dr Valery S. Lesovik
naukavs@mail.ru

Belgorod State Technological University named after V.G. Shukhov
Institute of Architecture and Construction
Kostykova str., 46 Belgorod RU

At present environmental problems of the North and the Arctic due to their natural and geographical peculiarities are likely to grow from regional to global scale that threatens to destabilize climatic, geochemical, cryolithological and ecological processes on a vast territory of the northern hemisphere. Problems of irrational nature management in the region are the core of numerous ecological problems of these districts. Meanwhile, this region is of strategic importance due to the richest raw-material base and vast free territories. Development of the North and the Arctic leads to the increase of anthropogenic burden on the environment taking into account its low capability of self-recovery. Moreover, it has a negative impact on the health of the population. At present we can ascertain the fact of connection failure in the equilibrium system “human – material – environment” in the structure of northern cities. Taking into account the territories of the North and the Arctic, the new scientific field called Architectural Geonics is one of the most relevant. It is aimed, first of all, at the improvement of people’s life conditions due to designing of buildings inherently fitting into the environment according to geomorphology, climate, and cultural traditions of the region. Issues of using environmentally friendly composite materials (composite binding materials, industrial waste, energy saving raw materials, etc.) are also important. The goal of this work is to improve the environmental situation in the Arctic region (by example of Arkhangelsk Region) by means of creating and using environmentally friendly composites in construction. Moreover, the use of anthropogenic waste of diamond industry as a raw material during production of concrete “green composite” allows decreasing ecological impact on the environment of the region, as well as increase diamond field mining profitability. The theoretical basis for solving the problem of rational development of the Arctic regions can be a new scientific field called geonics (geomimetics).

Polymeric resin obtaining of polystyrene reuse with applicatin in mortar

R.M. Arredondo Ramírez¹, M.I. Espitia Cabrera¹, R. Soto Espitia CAPUFE², M.E. Contreras García³
iesumich@yahoo.com

¹Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, México

²Caminos y Puentes Federales, Cuernavaca, México

³Instituto de Investigaciones Metalúrgicas, Universidad Michoacana de San Nicolás de Hidalgo

Current accumulation of solid waste in landfills and urban pollution is a growing problem that brings environmental consequences. The importance of developing sustainable processes where polymeric materials such as polystyrene of reuse, not only provides environmental benefits, but also brings news industries associated with obtaining income and employment generation. The application of this reuse material is applied in one of the most important areas of development: the construction. A novel resin has been manufactured from post-consumer polystyrene, and when is used as an additive for mortar mixtures improved the mechanical properties and performance in comparison with and unmodified mortar mixtures.

In order to obtain the resin, the expanded polystyrene (EPS) (density 17 kg/m³) has been solved in ethyl acetate to achieve a solution with specific characteristics of workability. This polystyrene solution has been mixed with water and soya lecithin as a template to formulate the resin at 35% weight of polystyrene. In the mix design of the mortar, the weight fraction of cement:sand was kept 1:3 and then it was mixed with water and resin to formulate the mortar modified.

Keywords: *Wasted expanded polystyrene; Modified Mortar; Polymer*

Effect of temperature and concentration of precursors on morphology and photocatalytic activity of zinc oxide thin films prepared by hydrothermal route

Saara Heinonen¹, Juha-Pekka Nikkanen¹, Matti Kannisto², Elina Huttunen-Saarivirta¹,
Hanna Hakola², and Erkki Levänen¹,
saara.heinonen@tut.fi

¹Department of Materials Science, Tampere University of Technology P. O. Box 589, FIN-33101
Tampere, Finland

²Department of Chemistry and Bioengineering, Tampere University of Technology P. O. Box 541,
FIN-33101 Tampere, Finland

Zinc oxide (ZnO) is an important semiconducting material due to its potential applications, such as conductive gas sensors, transparent conductive electrodes, solar cells, and photocatalysts. Photocatalytic activity can be exploited to decompose hazardous pollutants from environment.

In this study, we produced zinc oxide thin films on a stainless steel plates by hydrothermal method varying the precursor concentration and the synthesis temperature (from 70 °C to 90 °C). Morphology of the synthesized films was examined using field-emission scanning electron microscopy (FE-SEM) and photocatalytic activity of the films was characterized using methylene blue decomposition tests and water contact angle measurements. It was found that the morphology of the nanostructures was strongly affected by the temperature and the precursor concentration of the synthesis. At lower temperatures zinc oxide grew as thin needle-like nanorods of uniform length and shape and aligned perpendicular to the stainless steel substrate surface. At higher temperature the shape of the rods transformed towards hexagon shaped units. The diameter of the hexagons increased as the temperature increased. The variation in precursor concentration lead to change from thin needle-like rods to flaky platelets, with the flake size growing up to micrometre scale. It was also observed, that the photocatalytic activity of the prepared films depended clearly on the changes in morphology of the surfaces.

Keywords: *zinc oxide, photocatalytic activity, hydrothermal growth, surface morphology*

Behavior and characterization of the colloidal suspensions

H Gouchene¹, A E Hadjadj²
gouchenehamid58@yahoo.fr

¹ National High School of Mining and Metallurgy, Annaba – Algeria

² Badji Mokhtar University, Electro-mechanics department, Annaba – Algeria

Colloidal suspensions are fine solid particles dispersed in a liquid medium; interaction between these very small particles is due to Brownian movement. Such systems have special properties which are of great practical importance. However colloidal suspensions can be found in many industries such as water treatment, drilling fluids, ceramics production, flotation etc... Physical and chemical properties of such colloids and suspensions are strongly dependent on the nature and width of the solid-liquid interface. One of the main questions asked by colloidal sciences is the dichotomy between theory and practice of the behavior of colloids kinetics. The present work is trying to understand the rheological and physico-chemical behavior of the colloidal suspensions and particles interaction mechanisms.

Keywords: *colloidal Systems, rheological Properties, Zeta potential, Solid-Liquid interface, colloidal suspensions.*

Polyvinyl alcohol-melamine formaldehyde resin composite and nanocomposites as antimicrobial films

Kalpana Madgula¹, Rita Kakkar¹, Y.V.Saritha Nehru¹, Pramod Kumar²
kalpanasekhar@yahoo.com

¹Department of Chemistry, St. Francis College for Women, Begumpet, Hyderabad 500016, India.

² Centre for Chemical Sciences and Technology, Institute of Technology,
Jawaharlal Nehru Technological University, Hyderabad. India

Melamine formaldehyde resin, MFR, was prepared by well known two stage process of melamine – formaldehyde reaction. In this study the reaction has been carried out to the first stage only at the pH of 9-10 and used as such. Thus prepared MFR resin was blended at about 80°C with 10% aqueous polyvinyl alcohol. The PVA-MFR condensation reaction was carried out in controlled condition. Nanoparticles of ZnO and TiO₂ were prepared and characterized. Each of the prepared nanosamples could be blended in PVA-MFR composite and the nanocomposite films, coatings, sprays were obtained. The composite films were subjected to TGA and antimicrobial studies. The PVA-MFR composite films and coatings on glass, Aluminium foil, clay pots, fabric, sponge etc are found to have a very high level of antimicrobial activity. Addition of any of the ZnO and TiO₂ nanoparticles enhance the antimicrobial activity of the material. The activity is very high, especially against very highly resistant gram positive bacteria like *S. Aureus* and Bacillus. Variation of antimicrobial activity with composition and concentration of nanoparticle used is being reported. The material is very stable and retains its activity over a period of time.

Keywords: MFR resin; PVA-MFR composite films; nanocomposite films; Characterization; Antimicrobial activity

Investigation of the Properties of Sb Doping on Tin Oxide SnO₂ Materials for Technological Application

Z. Hachoun¹ ; A Ouerdane^{1,3}; M.Bousslama², M.Ghaffour², A.Abdellaoui², Y. Caudano³
 Hachoun_zoubir @yahoo.fr; ouerdanea@yahoo.fr

¹Université de Khemis Miliana, Route de Theniet El Had 44225 KH-Miliana W. Ain Defla Algeria

²LabMat Ecole Nationale Polytechnique d'Oran Mnaouer Oran 31000 ; Algeria

³ Université de Namur Rue de Bruxelles, 61B-5000 Namur, Belgium.

The assemblies of nano-SnO₂/SiO₂ , Sb-doped -doped nano-SnO₂/SiO₂ in which the nano-SnO₂ particles are located in the pores of mesoporous SiO₂ were prepared using spray technique and investigated owing to XPS X-ray Photoelectron (fig.1) Spectroscopy the Auger Electron Spectroscopy (AES (EDS)) fig.2, Electron Energy Loss Spectroscopy (EELS) fig.3 Electron Diffusion spectroscopy spectroscopic techniques associated to the simulated method casino scanning microscopy (SEM) fig.4. Many samples were analyzed one by one in order to find the best conditions giving rise to crystals Sb-SnO₂ with small grains needed for technological applications. With increasing the weight ratio of SnO₂:SiO₂ or the weight ratio of Sb:Sn , the annealing temperature, our samples are of large and small grains distributed with different homogeneity on the surface. Transmission Electron micrography (TEM) has been used for particles size determination along all our samples investigation fig.2. Optical and electrical properties were computed or measured using appropriate tools and finally the status of the issue on doping and on the properties acquired for Sb doping is highlighted

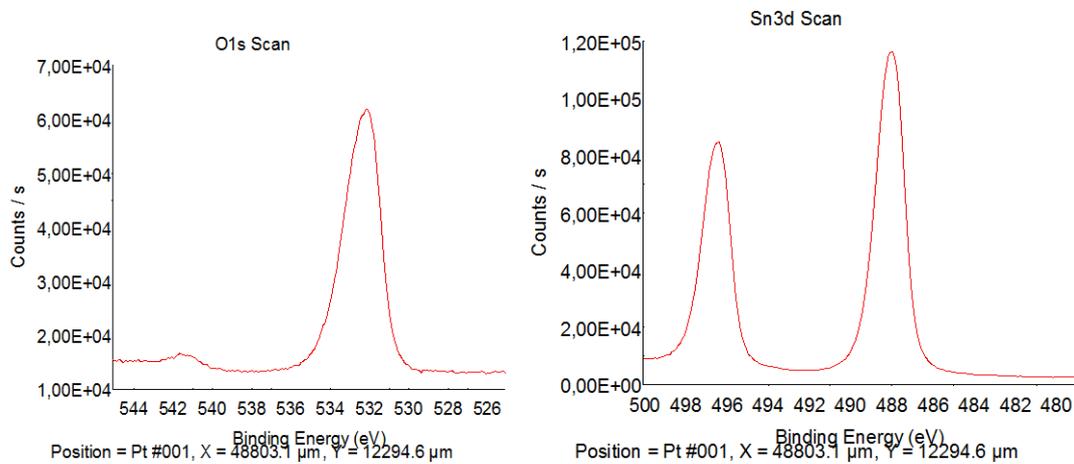


Fig.1 Scan XPS of O1s and Scan XPS of Sn3d of SnO₂ compound

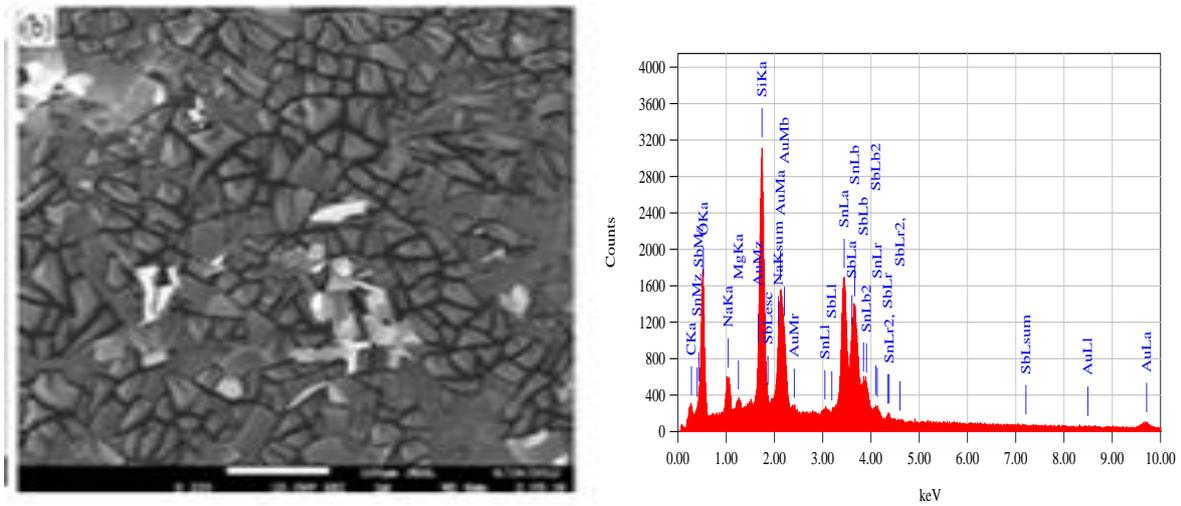


Fig.2 TEM image showing grain formation on the SnO₂ surface (left) and EDS spectroscopy giving rise to element energy position of SnO₂ doped antimony on SiO₂ substrate (right)

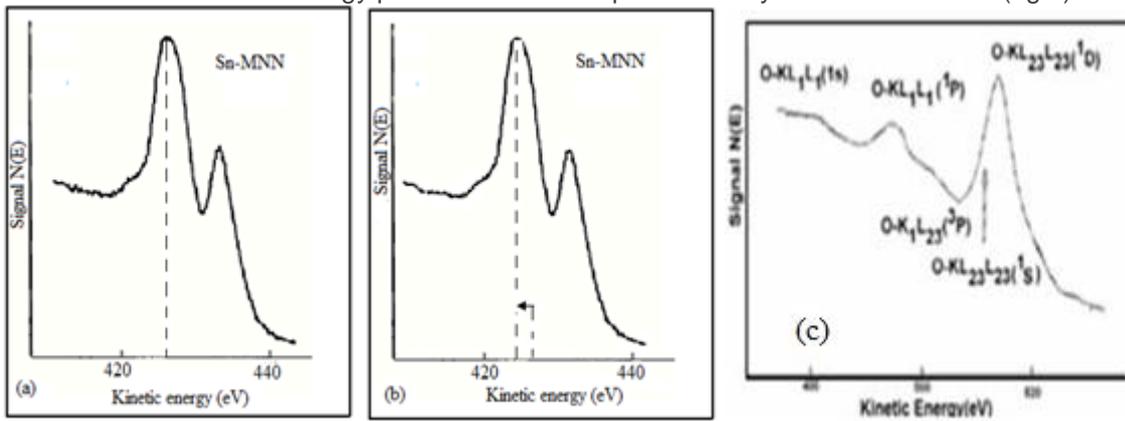


Fig.3 AES spectra of Sn and oxidized Sn showing the shifting to low AES energy (left) and the O-KLL of SnO₂ (right)

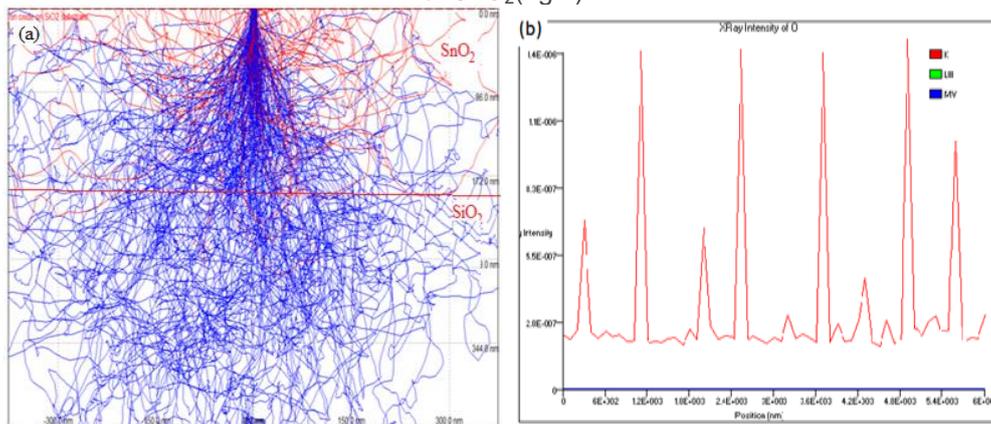


Fig.4. Casino scanning simulation of SnO₂ on SiO₂ substrate showing the distribution of the grains on the SnO₂ surface.

Investigation of InGaAsN Compound for use as Laser Diode

A.Ouerdane
ouerdanea@yahoo.fr

Université de Khemis Miliana route de Theniet El Had 44225 Algérie

The InGaAsN/GaAs material system has recently been investigated as material for the realization of high-performance laser diodes emitting at the optical fiber window. Nitrogen content in GaAsN has a great influence on the band gap in this semiconductor. The knowledge of influence of nitrogen on optical transition energies in GaAsN/GaAs quantum well structures is very important due to the possibility of adjustment of the optical transition energies to the telecommunication wavelength range when the system InGaAsN is submitted to further indium elements giving rise to the quaternary alloys (In)GaAsN. The purpose of this work is to solve the coupled nonlinear rate equations describing the complex electric field and the carrier density in a simple model of the $\text{GaN}_x\text{As}_{1-x}$ or (In) GaAsN semiconductor laser. The model is sufficient to account for many of the observed dynamics in a single mode semiconductor laser in response to a dynamic drive current, such as relaxation oscillations and frequency chirping.

Keywords: *laser semiconductor, GaAsN, (In)GaAsN, rate equations, telecommunications*

Chemical synthesis and Dielectric properties of polyaniline/TiO₂ nano composites

L.N.Shubha¹, P.Madhusudana Rao¹, M.Kalpana²
Shubha_su@rediffmail.com

¹ Dept. Physics, J.N.T.U, Hyderabad, AP, India
² Dept. Chemistry, St. Francis College, Hyderabad, AP, India

Polyaniline / titanium di-oxide (PANI / TiO₂) Nano composite was prepared by insitu chemical oxidation polymerization method. The synthesis involved the formation of dark green colored Polyaniline-TiO₂ nanocomposite. The Nano composites were characterized by FTIR, TEM, XRD, and UV-Visible Spectroscopy. The expected structure of polymer was confirmed by the characteristic peaks in FTIR and UV-Visible spectra. The XRD pattern shows the monoclinic structure of the composite. TEM image indicated that the TiO₂ nano particles were well dispersed in polymer matrix. TGA curves show that the thermal stability of polymer nano composite is around 650⁰C. The A.C. conductivity, dielectric constant ($\epsilon'(\omega)$) and Dielectric Loss ($\epsilon''(\omega)$) of PANI /TiO₂ nano composite were measured using impedance analyzer. The effect of doping on the dielectric properties was investigated.

Keywords Polyaniline/titanium di-oxide (PANI/TiO₂) Nanocomposite; AC- Conductivity; Dielectric Constant; Dielectric Loss.

f

SESSION 12

Novel Synthesis and Processing Technology

Preparation of hydroxyapatite/nanofibrous boehmite composite hollow spherical particles by spray drying

Takeshi Toyama¹, Tetsuya Kodaira², Naofumi Nagai³, Fujio Mizukami^{2,3} and Nobuyuki Nishimiya¹
toyama.takeshi@nihon-u.ac.jp

¹Department of Materials and Applied Chemistry, College of Science and Technology,
Nihon University, 1-8 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan

²National Institute of Advanced Industrial Science and Technology (AIST),
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

³Kawaken Fine Chemicals Co., Ltd.,
2-3-3 Nihombashi, Horidome-cho, Chuo-ku, Tokyo 103-0012, Japan

The spray-drying method is a process in which an aqueous solution containing dissolved materials is sprayed into a furnace and the materials are instantly dried to form powder. Hollow spherical particles are prepared using this method. Hydroxyapatite (HAp) has good biocompatibility and good ion-exchange and adsorption properties; therefore, HAp is a very important material. We succeeded in preparing highly-concentrated HAp solutions by blowing CO₂ into HAp suspensions. We then prepared HAp hollow spherical particles from those solutions by spray drying. However, the obtained particles could not be used as biomaterials, adsorbents, fillers, and so on because the mechanical strength of the particles were very weak. Therefore, we considered the use of boehmite nanofibers (the minor axis: 4 nm, the major axis: 1400 nm) in order to improve the mechanical strength. We considered that the hollow spherical particles could be prepared from a highly-concentrated HAp solution that included boehmite nanofibers by spray drying. In the present study, we investigated the preparation of a HAp/nanofibrous boehmite composite hollow spherical particles by spray drying and their mechanical properties.

When a HAp solution containing 0–0.05 mass% of boehmite nanofibers was spray dried at 100°C, hollow spherical particles 1–2 μm in size were obtained. Also, it was suggested that the nanofibers were incorporated into the walls of the hollow spherical particles, since the nanofibers were not clearly observed on the particle surfaces. The compressive strength of the obtained particles was assessed by measuring the compressive strength of each particle. While the compressive strength of the HAp hollow particles without the boehmite nanofibers was approximately 0.6 MPa, the one of the composite particles was enhanced to approximately 8.5 MPa by the addition of 0.05 mass% of boehmite nanofibers.

Keywords: *spray drying, hollow spherical particles, hydroxyapatite, boehmite, mechanical properties*

Preparation and mechanical properties of II-gypsum anhydride hollow spherical particles by spray drying

Masato Miyauchi, Takeshi Toyama and Nobuyuki Nishimiya
toyama.takeshi@nihon-u.ac.jp

Department of Materials and Applied Chemistry, College of Science and Technology,
Nihon University, 1-8 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan

Gypsum is used mainly as gypsum board and has been widely studied for the functionalization of gypsum board. A functional gypsum board is prepared by adding functional material to the gypsum board. However, functional gypsum boards have several problems. The main problem is the affinity between the gypsum board and functional materials, which may lead to a decrease in the mechanical strength of the gypsum board. To address this, we focused on the spray-drying process. We have reported on the preparation of hollow spherical particles of various compositions, furthermore spray-drying could be included in the other component inside^[1]. Thus, if gypsum hollow spherical particles are prepared by spray drying, functional materials can be encapsulated inside. However, to use these particles as a filler, an evaluation of their mechanical strength is necessary. Therefore, in the present study, we prepared II-gypsum anhydride hollow spherical particles by spray drying and evaluated their compressive strength.

Gypsum hollow spherical particles were produced by spray drying from a gypsum solution. The obtained product was a white powder with spherical particles of 1–5 μm size; the thickness of the particle wall was approximately 0.18 μm . The hollow spherical particles were confirmed to be β -gypsum hemihydrate. However, these particles were unstable in water. Therefore, the powder was calcined for 1 h at 500°C to obtain stable anhydride gypsum. The resulting powder particles retained their hollow and spherical structure. Then, the obtained particle was measured by compressive strength of only one particle. The compressive strength of the as-fabricated particles was approximately 4.5 MPa. However, the compressive strength of the product after calcination decreased approximately 3.1 MPa.

Keywords: *gypsum, spray drying, hollow spherical particles, functional material*

Initiation of the Adiabatic Wave of Combustion for Obtaining the Substances with the Free Valence

Anna Baideldinova¹, Georgy Ksandopulo ¹ and Kainzhamal Omarova²
abaid@inbox.ru

¹Institute of Combustion Problems, Almaty, Kazakhstan

²Chemical Department of the Kazakh National University

According to the stated goal of obtaining substances with the free valence for the linkage of the nano-powders, the procedure of the synthesis of materials under the extreme nonequilibrium conditions is developed. The combustion of multilayer aluminothermic systems in the revolving reactor was investigated. Experiments were carried out in the reactor of high-temperature centrifuge. The frequency of rotation varied from 500 to 2500 rev./min. The initiation of process realizes by electric pulse in the effective layer. Further the wave of combustion was propagated along the axis of the reactor. The macrokinetic characteristics of the combustion wave, which is developed in the exothermic mixtures of aluminum with oxides of tungsten, iron and copper are determined. The particles of the reduced metal penetrated the underlayers of fresh mixture under the action of centrifugal acceleration and created the additional centers of ignition. Summary thermal and kinetic energy of the flow of metallic particles exceeds tensile energy of chemical bond.

It is shown that the process of combustion can be transferred into the adiabatic regime under the action of centrifugal acceleration. Heat energy dispersion through the walls of reactor is negligibly as compared with the released heat energy in the process of self-propagating high-temperature synthesis. In addition, inside the system energy grows due to an increase in the kinetic energy of the particles.

The arrangement of the layer of inert substance on the way of the adiabatic wave of combustion leads to change its structure. Energy of the adiabatic wave of combustion was used also for the initiation of reactions with the high energy barrier. As a result the complex oxide compound Al₂₀B₄O₃₆ was obtained. The presence of free radicals in it is confirmed by the method EPR.

Keywords: *combustion, centrifugal acceleration, high-temperature synthesis, adiabatic wave, the free radicals*

Mechanochemical initiation of SH-Synthesis of Sialon Containing Ceramic Systems

Nina Mofa, Zulhair Mansurov, Bakhtiyar Sadykov, Zhandarbek Sabayev
Nina.Mofa@kaznu.kz

Combustion Problems Institute, al-Farabi Kazakh National University, 172 Bogenbay Batyr st.,
050012 Almaty, Republic of Kazakhstan

Sialons, due to their corrosion resistant properties even at temperatures up to 1400°C, are promising materials for using them as refractories and building materials. In this work, sialon containing ceramic materials were obtained under the conditions of self-propagating high temperature synthesis (SHS) in the atmosphere of air using quartz pretreated in mills-activators of a dynamic action. Mechanochemical treatment is one of the methods to change considerably the structure and state of the material being treated and, hence, increase its chemical activity. It is shown that formation of definite structures or a film from organic compounds makes it possible to encapsulate the energy state of the treated material. Destruction of the shell-capsule directly in the course of SHS on the preactivated material will allow to most fully realize the energy saved during mechanical treatment of the substance. With a definite composition of the capsule, the products of its decomposition interacting with the main reagent of the system contribute to creation of SHS-material of the required composition, structure and properties.

The increased chemical activity of the system (SiO_2+Al) results in formation of sialons $\text{Si}_{6-z}\text{Al}_z\text{O}_7\text{N}_8$ ($0 < z < 4,2$) instead of mullite in the reaction products. Introduction of carbon containing components into the mixture composition provides creation of a reducing atmosphere in the sample volume. The decrease in the amount of active oxygen in the mixture due to formation of carbon oxide contributes to a more active interaction of aluminium with nitrogen of air. The reactions between the charge components and intermediate products of the reaction with participation of carbon and nitrogen of air result in production of sialon in the composition of ceramics being synthesized.

Keywords: SH-synthesis, mechanochemical treatment, sialon

Self-Propagating High Temperature Synthesis of High Porous Ceramics on the Basis of Natural and Technogenic Raw Materials

Zulhair Mansurov, Nina Mofa, Bakhtiyar Sadykov, Zhandarbek Sabayev
Nina.Mofa@kaznu.kz

Combustion Problems Institute, al-Farabi Kazakh National University, 172 Bogenbay Batyr st,
050012 Almaty, Republic of Kazakhstan

To conserve heat energy in the operating space of thermal high temperature sets and prevent its outflow to the environment, special materials-high temperature heat insulators are necessary. For high temperature heat insulation, mainly, microporous materials based on calcium aluminates and silicates produced by different methods are used. Self-propagating high temperature synthesis (SHS) is one of the most effective methods of creating such materials and items on their basis.

For SHS, different quartz containing systems including natural quartzites as well as industrial wastes (fly ash, aerated concrete) subjected to mechanochemical treatment (MCT) with different modifying additives are used. Modifiers are stated to play an important role in the change of structural characteristics and configuration of the forming objects, the change of the surface modified layers of particles being dispersed in the process of MCT.

It is shown that MCT in the presence of modifiers of natural minerals and technogenic raw materials used as components of the charge mixture for SH-synthesis of composition systems contributes to the change of kinetic characteristics of the combustion process (reduction of the induction period of ignition and the increase in the combustion rate) and provides maximum formation of corundum and aluminosilicate compounds. During MCT of complex charge mixtures, modifying additives provide formation of a high porous structure of SHS-material being synthesized.

The presence of fly ash and aerated concrete in the composition of SHS-charge contributes to production of the porous and refractory material with a high strength (up to 80-100 MPa). The samples modified in the process of MCT with polystyrene have a fine porous structure with dense partitions, that is most promising for using such materials for production of heat insulation systems.

Keywords: *SH-synthesis, mechanochemical treatment, high porous ceramics*

Fabrication of Dense and Precise Ceramic Parts by using Novel Additive Manufacturing Technologies

Johannes Homa¹, Martin Schwentenwein¹
jhoma@lithoz.com

¹Lithoz GmbH, 1040 Vienna, Austria

Today, Additive Manufacturing (AM) technologies are already established in the plastic and metalworking industry; however, the ceramic industry has very rarely used this kind of technology for their purposes. Nonetheless, there is a strong need for the introduction of AM technologies, because no appropriate prototyping technologies exist and the tools for powder injection molding are very expensive. These are actually perfect conditions for the implementation of AM technologies, but since ceramic materials are used where other materials fail, the quality and the reliability of the parts are crucial which used to limit the applicability of the AM approach for ceramics.

In this paper a novel AM-technology is presented, which is capable of producing strong, dense and accurate ceramic parts, the so-called Lithography-based Ceramic Manufacturing (LCM) process. LCM is a slurry-based process, where a photocurable monomer system is mixed with ceramic powder and selectively hardened through mask exposure to initially give the so-called green parts. This green parts are basically composites of ceramic particles within a photopolymer matrix. Upon thermal post-treatment the organic matrix is removed. The resulting voids and pores are subsequently eliminated during sintering to give the dense ceramic bodies which exhibit equal properties to conventionally formed ceramics; alumina parts fabricated by this new technology exhibited a theoretical density of 99.3% and 4-point bending strength over 430 MPa.

This establishment of a new production methodology for ceramic parts by the LCM process enables the structuring of strong and highly complex structures, holes with diameters of approximately 250 μm and structures with a strut thickness of below 200 μm are feasible by this technology. Moreover, it also allows the economical production of small scale series or even individual parts. These opportunities make LCM an interesting and capable alternative to conventional processing techniques for the ceramic industry.

Keywords: *Additive Manufacturing, high performance ceramics, alumina, zirconia, photopolymerization, lithography*

Study on the Phase Formation of Ceramics Obtained by Combustion Syntheses and Ball Milling

H. Boutefnouchet¹, C. Curfs²
hboutef69@yahoo.fr

¹Laboratory of magnetism and spectroscopy of solids (LM2S) Badji Mokhtar University, B.P. 12, 23000 Annaba, Algeria

²European Synchrotron Radiation Facility (ESRF), B.P. 220- F- 38043 Grenoble, France.

The search for new materials is a technical and economic requirement, especially for electro mechanics and aeronautics sectors that are demanding more efficient materials, particularly products that combine the characteristics of wear resistance, hardness, resistance to high temperatures, etc... with as low as possible production cost.

The need to develop new materials is closely related to their manufacturing method. This study presents advanced techniques in the synthesis of new ceramic materials such as SHS (self-propagating high temperature synthesis), TES (thermal explosion synthesis) and MA (mechanical alloying). Processing techniques which become competitive with conventional processes.

Products obtained by these different techniques of elaboration are characterized by time resolved X-ray diffraction (TRXRD) and scanning electron microscopy (SEM) to determine the nature of the different phases that make up these materials.

Keywords: *titanium carbide; combustion synthesis; NiO-Al system; Ball milling*

A Synthesis Method of Stoichiometric Calcium Oxide Stabilized Zirconia Nanopowders for Ca-TZP Ceramics

Anna Łabuz¹, Waldemar Pyda¹, Radosław Lach¹
alabuz@agh.edu.pl

¹Department of Ceramics and Refractories, Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Cracow 30-059, Mickiewicz Avenue 30, Poland

Several studies on preparation of CaO stabilized zirconia nanopowders have suggested that calcium ions do not incorporate quantitatively into the zirconia lattice during the formation of CaOZrO₂ solid solutions under hydrothermal conditions, and therefore remaining calcium species are removed from the system during washing with water. Some losses of calcium from calcined powders in the CaO-ZrO₂ system are also present, especially when precursors used force application of the water washing stage and calcination temperatures are too low for full incorporation of calcia into the zirconia solid solution, as in the case of nanopowder preparation routs. So, the aim of the present work was to develop a method of preparation of CaO-ZrO₂ nanopowders, avoiding losses of calcium ions. Calcination of a physical mixture of zirconia gel and calcium hydroxide was employed, as the method with no the water washing stage. The chemical composition of the precursor mixture permitted to obtain the zirconia s.s. nanopowder partially stabilized with CaO. The mixture was wet homogenized and dried, and then calcined for 1 h at 500 °C. The behaviour of the mixture of precursors was studied by the DSC/TG method. The phase and chemical compositions of the resultant nanopowder were determined by X-ray diffraction and X-ray fluorescence analyses, respectively. Laser diffraction and nitrogen adsorption (BET) methods were used to characterize a degree of size reduction of the nanopowder. The densification ability of the nanopowder during compaction and sintering was determined based on compaction and dilatometric curves and mercury porosimetry measurements. The phase composition, density and mechanical properties of sintered bodies were determined. The CaO-ZrO₂ nanopowder with tetragonal symmetry and nanosized crystallites was obtained. Effects of the proposed method on properties of calcia-zirconia nanopowders and their applicability for manufacturing Ca-TZP ceramics are discussed.

Key words: powder synthesis, ZrO₂, CaO, calcination, densification, tetragonal zirconia polycrystals

Synthesis and Properties of Heat-resistant Ceramics Based on Al_2O_3 with Addition of MgO

Yuriy Kreto¹, Svetlana Buyakova^{1,2,3}, Bogdan Gimaev², Sergey Kulkov^{1,2,3}
kretov2005@yandex.ru

¹ National research Tomsk State University, Lenin str., 36, Tomsk, 634050, Russia

² National research Tomsk Polytechnic University, Lenin str., 30, Tomsk 634050, Russia

³ Institute of Strength Physics and Materials Science of the SB RAS, Akademichesky str. 2/4, Tomsk, 634021, Russia

It is well known that high temperature alumina ceramics are great interest for creation of high quality materials with different high-temperature properties, which can be monitored and controlled by different additives like magnesia.

In this work ceramic based on alumina and magnesia with wide magnesia content was studied in a wide temperature range. It has been shown that while increase a content of MgO were observed an increase of shrinkage. By using X-ray analysis it was found that in samples with 30-50% content of MgO, aluminum-magnesium spinel formation occurs (MgAl_2O_4), which has a very high melting point, chemical resistance, strength and hardness. It has been studied mechanical properties of sintered materials and its connection with microstructure and phase content.

Keywords: *Thermal resistance, wear resistance, toughness, crack resistance, shrinkage, porosity, and spinel.*

Properties of Sintered $ZrO_2 - Al_2O_3$ Ceramic Prepared from Zirconia and Alumina Nanopowders

V. Promakhov, I. Zhukov, S. Kulkov.
vvpromakhov@mail.ru

Institute of Strength Physics and Materials Science SB RAS, 634021, Russia, Tomsk
National Research Tomsk State University, 634050, Lenin Pr. 36, Russia, Tomsk
National Research Tomsk Polytechnic University, 634050, Lenin Pr. 30, Russia, Tomsk

Ceramic composites zirconia - alumina has a high mechanical properties. These materials are widely used for different applications. In this study were obtained composites $ZrO_2-Al_2O_3$ mixture from zirconia powder and 20 % Wt alumina powder. The crystal size of alumina powder - 40 nanometers, the zirconia - 20 nanometers. The zirconia powder was only in the tetragonal modification and alumina powder has alpha-modification with content about 99.5 %. Mixing of powders produced by ball milling process and pressure for cold mould was not more than 100 MPa. Sintering compacts produced at 1500 °C. It has been found that under these conditions the sintered composites has residual porosity approximately 3 - 5%. According to XRD analysis of the sintered ceramics contain only alpha phase alumina and tetragonal phase zirconia. Grain size does not exceed 0.8 μm , the crystallite size of less than 80 nanometers. Three point bend strength achieve 600 MPa, $K_{IC} = 12 \text{ MPa} \cdot m^{1/2}$, elastic modulus of 350 GPa.

Keywords: *zirconia, alumina, composites, mechanical properties.*

Financial support by Grant President RF MK - 5681.2014.8; MK - 5883.2014.8. RFBR grant HK 14-08-31087\14.

Pyrolysis of Blends of Waste Tyre and Coal Fixed Bed Reactor

Özlem Onay
oonay@anadolu.edu.tr

Anadolu University, Porsuk Vocational School, 26140 Eskisehir, TURKEY

Relevant advantages in the utilization of alternative fuels may lead to gradual replacement of the overuse of the traditional fossil fuels. Used tires represent a valuable source of energy and material products; however, at the same time they are also a potential threat to the environment. Thus, recycling of waste tires accompanied by recovery of material or energy is important from both economical and ecological viewpoints. Waste tire an ideal material for pyrolysis and combustion as well as for gasification, because of waste tires possess high amount of carbon with high heating value. Pyrolysis is a process that allows the decomposition of waste tyre into solid char, pyrolytic oil, and gases which may be used as fuels or as feedstock for petrochemicals and other applications. Distribution of material into the pyrolysis yields and also composition of individual fractions are depended on the composition of the feed material, used pyrolysis technique and process conditions applied.

This study investigated potential synergistic activities between waste tire and coal during co-pyrolysis. The pyrolysis of different blends of waste tire with coal was carried out in well-swept fixed bed reactor, and over a range of pyrolysis temperatures between 400°C and 700°C, in order to compare the yield and characteristics of the products obtained. At the lower blending coal ratio conditions, the oil yields are higher than the expected ones, calculated as the sum of oil fractions produced by pyrolysis of each separated component. The maximum pyrolysis oil yield was obtained with 5% of coal mixed with waste tire. The obtained oils are characterized by FTIR, ¹H NMR, GC-MS and elemental analysis. The considerable synergetic effects were observed during the co-pyrolysis in a well-swept fixed bed reactor leading to increase in oil yield. These findings can potentially help to understand and predict the behavior of waste tire/coal blends in practical liquefaction systems.

Keywords: Co- pyrolysis; Biomass; Coal; Oil

Centimeter-long SiC nanowires: synthesis, characterization and growth mechanism

Xiaodong Zhang^{1,2}, Joachim Bollmann², Xiaoxiao Huang¹, Guangwu Wen¹
zhangxiaodong@hit.edu.cn

¹School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

²Institute of Electronic and Sensor Materials, TU Bergakademie Freiberg, Freiberg 09599, Germany

Silicon carbide (SiC) nanowires have been extensively studied in recent years because of their prospective applications in field-emitters, electronic or optical nanodevices, and reinforcements in composites. Kinds of approaches have been explored for the synthesis of SiC nanowires. However, the nanowires synthesized by these methods have typical lengths in the micrometer range (most of them are no longer than 1 μm). Moreover, if centimeter-long SiC nanowires can be synthesized, they should be much more useful compared to short nanowires for some specific purposes, such as field-emission (FE), device interconnects, and reinforcing fibers in composites.

In this work, we design a novel method to fabricate the ultra-long SiC nanowires via a simple low-cost route. As shown in Fig.1, SiC nanowires have the length of more than 1 cm, which could be the longest SiC nanowires that have been ever reported. The morphologies and crystal structures were determined by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The results show that the as-synthesized nanowires are β -SiC single crystalline with diameter range about 100 nm, lengths of tens of micron and the growth direction along [111]. And the possible growth mechanism of SiC nanowires is proposed. The centimeter-long SiC nanowires are very promising for applications and will be subject of further investigations.

Keywords: SiC nanowires, centimeter-long, synthesis, characterization, growth mechanism, potential applications

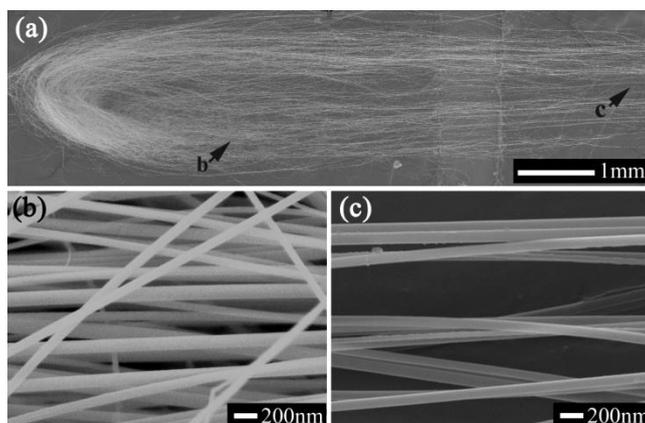


Fig.1 SEM images of the SiC nanowires

Structure and Mechanical Properties of Al – ZrW₂O₈ Composites

Vladimir Shadrin¹, Elena Dedova² and Sergey Kulkov^{1,2}
vshadrin91@gmail.com

¹Tomsk State University, 634050 Tomsk, Russia

²Institute of Strength Physics and Materials Science SB RAS, 634021 Tomsk, Russia

Zirconium tungstate (ZrW₂O₈) is one of the most promising materials for use as strengthening particles in metal matrix composites due to isotropic negative thermal expansion behavior in the temperature range of –270 to 770 °C which can stimulate the strengthening effect due to the formation of internal compressive stresses caused by thermal expansion difference between the matrix and reinforcement.

Al – ZrW₂O₈ composites were obtained by cold pressing and sintering processes at 600 °C in air for 1 h of aluminum and ZrW₂O₈ powder obtained by hydrothermal synthesis.

The SEM analysis showed that on the polished surface of specimens there are white particles with average size varied from 0.5 μm in the Al – 0.1 wt.% ZrW₂O₈ composite to 1 μm in that of Al – 10 wt.% ZrW₂O₈. The EDAX analysis showed that these particles contained Zr, W and O atoms in good agreement with stoichiometry of the ZrW₂O₈ compound (Zr:W=1:2). From the XRD analysis it was shown that only peaks corresponding to cubic aluminum and cubic zirconium tungstate were observed. The obtained lattice parameters of aluminum and ZrW₂O₈ slightly disagree with the literature, which may be due to microalloying of the matrix because of interaction during sintering process or due to presence of internal residual stresses in the material, in a second case compressive stresses in matrix can achieve 260 MPa.

The uniaxial compression and Vickers hardness tests were performed to examine mechanical properties of the composites. It was found that the Al–0.1 wt.% ZrW₂O₈ material demonstrated a 25% increase in their strength properties compared to pure aluminum.

Keywords: *zirconium tungstate, negative thermal expansion, aluminum, composites, strengthening*

Combustion of Layers Inorganic Systems under Rotation to Produce Composite and Gradient Materials

B.Zh.Nurakhmetov¹, A.E.Sergaziyev¹, N.U.Sabirov¹, A.N.Baideldonova², K.I.Omarova¹,
G.I.Ksandopulo²
abaid.@inbox.ru

¹Chemical department of the Kazakh national university

²Institut of Combustion problems, Almaty, Kazakhstan

Combustion is the sequence of exothermic physico-chemical reactions process of converting the initial reagents to different composition and structure products. Self-propagating high-temperature synthesis (SHS) is a one of the process of combustion. Self-propagating high-temperature synthesis (SHS) is a method for producing inorganic compounds by exothermic reactions. SHS technology has allowed by now more than 1,000 synthesize various inorganic compounds, materials and products. This process organization the reactants are used in solid form of powders, are mixed in certain proportions and compacted. This process is organized as solid powders are mixed in certain proportions and compacted. Combustion wave is initiated by a chemical or thermal pulse in the finished mixture which passes along the specimen at a speed of 0.1 - 20 cm / s. As a result, finished products are produced.

In our experiments oxides made in the form of powders, as WO₃, NiO, MoO₃, Co₃O₄, Fe₂O₃. We used aluminum powder as a reductant. As a result, reduction of the metal from its oxide we obtained metal ingot and corundum α-Al₂O₃.

Further goal was set - the study of complex multicomponent oxide combustion systems for obtaining composite and gradient materials. For this purpose, the combustion process of bilayer systems was investigated, including low calorie layer based on the this reaction



and high calorie layer based one second (2) reaction



Of course with the addition of Al₂O₃ in the initial mixture as ballast to slow down this extremely active and explosively process.

Experiments were carried out in the high centrifuge created and patented by our laboratory. Rotation speed in this study ranged from 1000 to 3000 rev / min, for the design and size of the plant corresponds to a change of centrifugal acceleration from 30 to 2000g. Combustion process in reactors recorded wit Nikon V1 camera at 400 frames / s.

Investigated the phase and chemical composition of the synthesis products Used the methods of optical microscopy, X-ray and X-ray diffraction, EPR, electron microscopy. With research combustion bilayer systems (81% WO₃ - 19% Al - 10% Al₂O₃, 56% B₂O₃ - 44% Al) composite material obtained

In the combustion process of multilayer systems (81% WO₃ - 19% Al - 30% Al₂O₃, 56% B₂O₃ - 44% Al, 81% WO₃ - 19% Al - 10% Al₂O₃, activated carbon, 56% B₂O₃ - 44% Al) obtained gradient material composition and structure, which gradually shifts from the metallic phase to the ceramic.

Thus, by self-propagating high-temperature synthesis in terms of rotation can get a different composition and structure of various materials. Combustion of different layers in the same conditions is an example. As a result were obtained, the gradient and composite materials.

Keywords: *combustion, high-temperature synthesis*

Kinetic study of non-isothermal decomposition of greek diasporic bauxite

Michail Samouhos¹, Panagiotis Angelopoulos¹, Maria Taxiarchou¹, Sergios Papageorgiou²
msamouhos@metal.ntua.gr

¹Laboratory of Metallurgy, School of Mining and Metallurgical Engineering, National Technical University of Athens, Zografou Campus, Athens, Greece

²Demokritos National Center of scientific research, Agia Paraskevi, Attiki, 153 10, Athens, Greece

Bauxite constitutes the major source of aluminum worldwide, while last decades, new, promising uses of bauxite in ceramics industry and as end-product in sintered form have been developed. For example, sintered bauxite, that is produced after bauxite calcination, is used as proppant in drilling of gas and oil from inconvenient deposits. Thermal processing is of great importance for ceramic products quality, while analysis and interpretation of decomposition phenomena during bauxite heating is hampered due to the presence of increased amount of associated minerals, namely, kaolinite, hematite, goethite etc.

In the present research work, non-isothermal decomposition of bauxite, originated from Parnassos mine, Greece, has been investigated. The sample consists mainly of diaspore and lower amount of gibbsite, hematite, anatase rutile and kaolinite. Fine grained bauxite samples have been heated under different heating rates (5, 10, 15, 20, 25 °C·min⁻¹) from ambient temperature up to 1000 °C. Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) methods have been implemented for the kinetic investigation of processes that take place during samples thermal treatment. It has been shown that, main transformations that take place during diasporic bauxite heating are diaspore and gibbsite dehydroxilation at 527 and 504 °C, respectively. Thermal decomposition of specific bauxite can sufficiently be described by the equation $da/dt = Ae^{-x}f(a)$ where a is the degree of conversion, A is the pre-exponential factor, $f(a)$ represents the mathematical expression of the kinetic model and $x = E/RT$ is the reduced activation energy, with E , R , T denote the activation energy, the universal gas constant and the temperature, respectively. Isoconversional method has been applied for the calculation of the activation energy, while the determination of the appropriate kinetic model has been performed after the calculation of $y(a)$ and $z(a)$ functions, where:

$$y(a) = (da/dt)e^x \quad \text{and} \quad z(a) = \pi(x)(da/dt)T/\beta$$

where $\pi(x)$ is the expression of temperature integral and β is the sample heating rate.

XRD, SEM and EDS characterization techniques have also been implemented for the chemical and mineralogical characterization of the bauxite sample and the identification of the processes that occur during its thermal treatment.

Keywords: diasporic bauxite thermal treatment, non-isothermal decomposition, Isoconversional method, thermogravimetry, differential scanning calorimetry

The Model Development for Composite Materials Synthesis in the Condensed Phase Taking Into Account Multi Scale Processes

Olga Kryukova¹, Anna Knyazeva^{1,2}
okruk@ispms.tsc.ru

¹Institute of Strength Physics and Materials Science of Siberian Branch Russian Academy of Sciences, 634021 Tomsk, Russia

²Tomsk Polytechnic University, 634050 Tomsk, Russia

Synthesis of composite materials could be carried out using the methods different in the ways of energy supply, the presence or absence of external fields, the ways of the reaction activation, in geometry, structure, and composition of the initial components. The synthesis processes are multiple-factor and labor-consuming. The mathematical methods are required to select the specific technology conditions and optimize the technology. In the literature ones distinguish the models describing the consuming transformations, the density and porosity evolution, the models of the mechanical behavior of powder materials and composites based on them; thermophysical models of the synthesis; the influence of external fields on the dynamics of porosity change; the sintering process description at the level of individual particles and evolved "mesovolumes" with some given initial structure.

In this paper we propose the model of composite material sintering under controlled heating, taking into account the peculiarities of new phase's formation in the reaction cell volume. With the help of the simplest version of the model, the algorithm of the interaction between two levels - the macroscopic (for the sample as a whole) and mesoscopic (at the level of individual particles surrounded by the melt) ones was debugged. Mathematical model of the sintering process includes the heat balance equation with term of external radiation heating (under the Stefan-Boltzmann law), the total heat from chemical reactions occurring in each reaction cell, the diffusion and chemical reactions in individual cells with the difference between the diffusion coefficient of mobile component in the phases. The proportion between the volumes of particle and matrix at start time gives the initial composition of the pressed sample. The number of cells follows from the proportion between geometrical sizes of particles and pressed sample. It is assumed that the chemical reaction rate depends on the temperature according to the Arrhenius law, on the concentrations according to the mass action law. The reaction parameters have been found in the literature or calculated using thermodynamic approaches. The temperature of the chamber walls is controlled by given law.

In general case, the reaction system has been written on the base of the phase diagrams of the chosen systems. The problem has been solved numerically.

Obviously, depending on the heating conditions, the initial composition of pressed sample, we obtain different composite structure. The synthesis process is characterized by the sample temperature dependence on the time, the concentration distributions of pure elements and new phase in the reaction cell and by the dynamics of average composition change in time. Average concentrations have been calculated integrating over the reaction cell.

This work has been performed under the program of fundamental research SB RAS, project II.23.2.2.

Keywords: *synthesis of composite, reaction cell, numerical modeling*

Surface Modification of Epoxy-Resin Taro Leaf Replicas via Cast Enlargement and Plasma Treatment

Miguel P. Ordoñez¹, Ivan B. Culaba²
mpordympordy@gmail.com

¹Materials Science and Engineering Program, Department of Physics, Ateneo de Manila University, Quezon City 1108, Metro Manila, Philippines

²Department of Physics, Ateneo de Manila University, Quezon City 1108, Metro Manila, Philippines

Direct polymer casting was performed, successfully replicating taro leaf (*Nelumbo nucifera*) surface microstructures responsible for superhydrophobicity onto an initially hydrophilic epoxy-resin medium through a simple, low-cost methodology. Contact angle measurement and scanning electron microscopy (SEM) were used to characterize the taro leaf, flat epoxy-resin surface, and replica. The taro leaf exhibited a 153° contact angle, while the flat epoxy-resin contact angle measuring 85° was improved by 66% to 141° in the replica, creating a near-superhydrophobic surface solely from change in surface morphology despite hydrophilic surface chemistry. This data was supplemented by roll-off angle measurement using a simple makeshift goniometer setup which revealed markedly different angles between the three: 9°, 63°, and 81° for the leaf, epoxy leaf replica, and flat epoxy respectively, as well as SEM data which revealed taro surface features replicated up to the 100 nm scale.

Replicas were then modified via physical and chemical means. Enlargement of surface morphology by 30% was achieved via application of tension during the thermoset gelation period, which caused a proportional 28% decrease in hydrophobicity from 141° to 102° due to micro and nanoscale spacing and feature expansion. Plasma treatment was conducted with argon gas at atmospheric pressure for an average of 20 seconds on original-scale samples, dramatically decreasing contact angle by 75% (from 141° to 35°), even lower than the flat epoxy surface, despite the intactness of the surface morphology as confirmed by SEM imaging. This data was supported by surface free-energy computation using the Lifshitz-van der Waals Acid-Base method with three different probe liquids, revealing a dramatic increase in polar groups, as well as FTIR-ATR spectroscopy revealing a slight decrease in C-H bonding.

Keywords: biomimetics, biomimicry, casting, polymer, taro, superhydrophobicity, microstructures, nanostructures, characterization, scanning electron microscopy, contact angle measurement, atmospheric pressure plasma jet, argon plasma, FTIR spectroscopy, instrumentation, goniometer

Micro and macro stresses in two level model of Ca-P coating growth

Nelly Nazarenko¹, Anna Knyazeva^{1,2}
n_nelli@mail.ru

¹Institute of Strength Physics and Materials Science of Siberian Branch Russian Academy of Sciences, 634021 Tomsk, Russia

²Tomsk Polytechnic University, 634050 Tomsk, Russia

The paper considers the model of growth of calcium phosphate coating on the implant micro arc method. The process of the coating formation includes the various physico- chemical steps and the transformation of the structure. From the experiments it was established that the coating consists of the following substances: 4 + titanium oxide, titanium pyrophosphate , calcium pyrophosphate, calcium titanofosfat. Presumably, they form in the volume of the porous coating and are accompanied by the diffusion of the ions through the growing layer. The deposition rate of the dispersed particles contained in the electrolyte (which could be the slurry) could be considered constant. The diffusion and chemical reactions proceed in different scale levels, and in the pores and in the bulk of the particles.

Macroscopic mathematical model includes the diffusion equations in the solid phase (in the substrate and in the growing coating) including the sources and sinks of substances in chemical reactions, the kinetic equations for the new forming substances, the symmetry condition, the boundary conditions at the fixed and moving boundaries, as well as the initial conditions.

To account for the formation of the coating structure the macroscopic model was supplemented by submodels of the diffusion in the vicinity of the structural elements. Their parameters are calculated on the base of the effective diffusion coefficients and formal kinetic parameters of the reactions for macromodel.

The problem on stress-strain state of structural elements with effective macroscopic mechanical properties is used to describe the stress-strain state of the sample with the growing coating. Macroscopic problem of mechanical equilibrium is solved in a standard way using the conditions of strain compatibility and the condition that the contour of the plate of the resultant force and moment of the resultant force.

The resulting problem is solved numerically. The calculations give the distribution of the concentration of substances in the surface layer of the plate, as well as the variation in the thickness and composition of the coating in time depending on the model parameters that characterize the experimental conditions.

This work has been performed under the program of fundamental research SB RAS, project III.23.2.1.

Keywords: *calcium phosphate, coating growing, micro and macro stresses*

Computer modeling and 3D printing technologies of ceramic parts with complex shape

Vasili Kovalev¹, Sergey Kulkov^{1,2}
Nakeed33@gmail.com

¹Tomsk State University, 634050 Tomsk, Russia

²Institute of Strength Physics and Materials Science SB RAS, 634021 Tomsk, Russia

Ceramic is a high-strength thermal-resistant material for different applications. There are many ways to manufacture it, but all the methods allow making simple shape only. Owing to slip casting complex shape can be achieved, but the casting mold creation problem is arises. It is well known that computer aided design and 3D printing technologies are developed very quickly and it allows to prototype details on computer and significantly reduce expenses on the early stages of development. The present work aims is development of complex shape casting molds with CAD and 3D printing technologies.

CAD system utilizes a parametric feature-based approach to create models and assemblies. 3D printing is achieved using an additive process, where successive layers of material are laid down in different shapes.

Digital model is obtained from CAD/CAE program SolidWorks, when 3D printer makes prototype model and finely silicon mold is obtained from printed detail. The data of receiving molds with different complex shapes is presented.

Keywords: *ceramic, casting molds, 3D printing, computer aided design*

Conversion Kinetic Scheme of Samarium Sulfate by Thermal Treatment

Elena Salnikova, Yuri Denisenko, Oleg Andreev
elenasalnikova213@gmail.com

Institute of Physic and Chemistry, Tyumen State University, 625000, Tyumen, Russia

The conversion kinetic scheme of samarium sulfate $\text{Sm}_2(\text{SO}_4)_3$ in hydrogen stream was plotted (fig. 1). Scheme reproduces presence of chemical compound, which was generated by behavior redox reaction between samarium sulfate and hydrogen. Availability of compound area $\text{Sm}_2(\text{SO}_4)_3$, $\text{Sm}_2(\text{SO}_4)_3 + \text{Sm}_2\text{O}_2\text{SO}_4$, $\text{Sm}_2(\text{SO}_4)_3 + \text{Sm}_2\text{O}_2\text{SO}_4 + \text{Sm}_2\text{O}_2\text{S}$, $\text{Sm}_2\text{O}_2\text{SO}_4 + \text{Sm}_2\text{O}_2\text{S}$, $\text{Sm}_2\text{O}_2\text{S}$ и $\text{Sm}_2\text{O}_2\text{S} + \text{Sm}_2\text{O}_3$ was showed on the scheme.

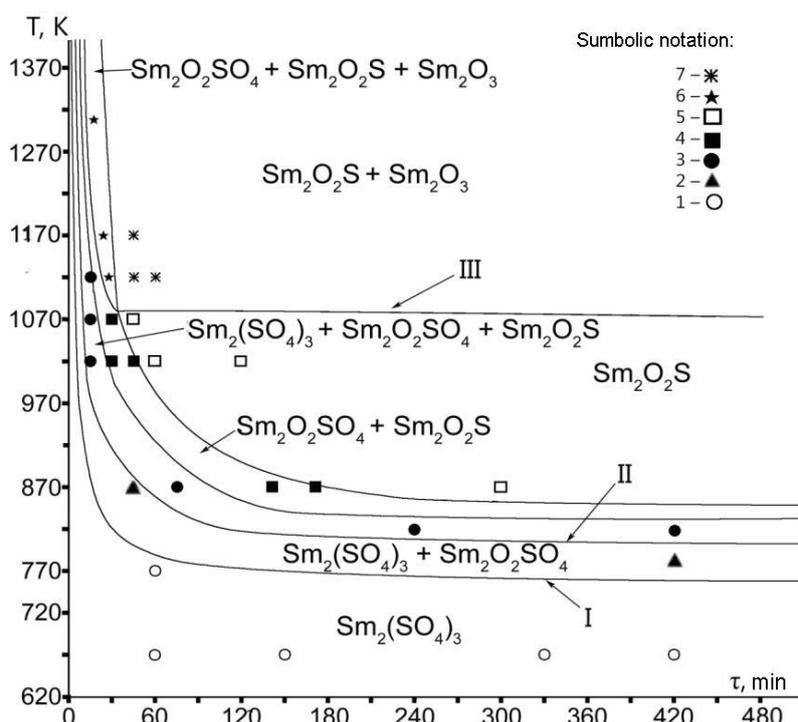
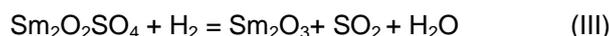


Figure 1. Conversion kinetic scheme of reactions at samarium sulfate $\text{Sm}_2(\text{SO}_4)_3$ treatment in hydrogen stream. Phase compositions: **1)** $\text{Sm}_2(\text{SO}_4)_3$; **2)** $\text{Sm}_2(\text{SO}_4)_3 + \text{Sm}_2\text{O}_2\text{SO}_4$; **3)** $\text{Sm}_2(\text{SO}_4)_3 + \text{Sm}_2\text{O}_2\text{SO}_4 + \text{Sm}_2\text{O}_2\text{S}$; **4)** $\text{Sm}_2\text{O}_2\text{SO}_4 + \text{Sm}_2\text{O}_2\text{S}$; **5)** $\text{Sm}_2\text{O}_2\text{S}$; **6)** $\text{Sm}_2\text{O}_2\text{SO}_4 + \text{Sm}_2\text{O}_2\text{S} + \text{Sm}_2\text{O}_3$; **7)** $\text{Sm}_2\text{O}_2\text{S} + \text{Sm}_2\text{O}_3$.

Equation of chemical reaction, which going on process samarium sulfate $\text{Sm}_2(\text{SO}_4)_3$ treatment in hydrogen stream was made:



The conclusion about temperature-time parameters of obtaining powder homogeneous samarium oxisulphide was made by analyze this scheme: in the temperature intervals 670-1070 K at time of treatment 180-480 minute and feed rate of hydrogen 1 ml/sec.

Key words: kinetic scheme, samarium oxisulphide.

Synthesis and Crystal Structure of α - and β -SrCeCuS₃

Anna Ruseikina, Semyon Koltsov
adeschina@mail.ru

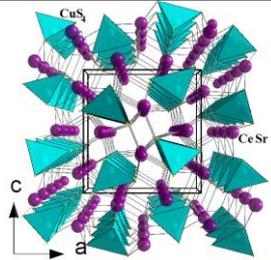
Chair of Inorganic and Physical Chemistry, Tyumen State University, 625003 Tyumen, Russia.

For the first time ever SrCeCuS₃-compound was synthesized by melting SrS, Ce₂S₃, Cu₂S in the ratio 2SrS:1Ce₂S₃:1Cu₂S in graphite open cup placed in vacuum sealed quartz ampoule. Then ampoule had been stoved to 1570 K and has been alloyed for 30 min. in electrical furnace. Cooling was run in furnace turned off. Samples stoved to 970 K had been alloyed in a vacuum sealed quartz ampoule for 4 months, stoved to 1170 K – for 2 months. Homogeneity of the phases samples was confirmed through physicochemical methods of analysis.

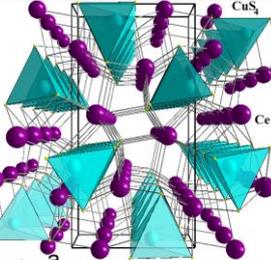
The use of derivative difference minimization method (there are anisotropic approximation for all atoms) and X-ray powder diffraction allowed clearer evaluation of the crystal structure of SrCeCuS₃. It has been found that there are two polymorphic modifications of rhombic system (space group of symmetry is *Pnma*): high-temperature modification, that's Ba₂MnS₃-structure type (ST) has elementary cell parameters are: $a = 8.1393(3)$, $b = 4.0587(4)$, $c = 15.9661(2)$ Å (alloying 1170 K) and low-temperature - ST BaLaCuS₃: $a = 11.1626(2)$, $b = 4.09697(5)$, $c = 11.5307(1)$ Å (Alloyed 970 K). In both modifications crystallographic positions of Sr и Ce is partially mixed (see the table 1 below), block-laminated organization is typical for both structure types. Along the b center-line there are chains made of CuS₄-distorted tetrahedrons. The one-capped of Sr/CeS₇ prism form a 3-D structure with channels accommodating copper ions.

Table 1. Atomic coordinates, site occupancies positions and thermal characteristics (Å²) in the structure of SrCeCuS₃. Geometrical projection [010] of the structure α - (a) и β -SrCeCuS₃ (b).

α -SrCeCuS ₃ (roasting 970 K)					
Atom	x	y	Z	Occupancy	U_{eq}
Ce1	0.48946(8)	1/4	0.31742(8)	0.842(3)	0.009(2)
Sr1	0.31784(12)	1/4	-0.00626(13)	0.842(3)	0.011(2)
Ce2	0.31784(12)	1/4	-0.00626(13)	0.158(3)	0.011(2)
Sr2	0.48946(8)	1/4	0.31742(8)	0.158(3)	0.009(2)
Cu	0.24429(20)	1/4	0.71176(20)	1	0.021(2)
S1	0.22318(30)	1/4	0.30637(34)	1	0.010(3)
S2	0.38485(36)	1/4	0.55674(33)	1	0.013(3)
S3	0.04962(28)	1/4	0.63951(29)	1	0.011(3)



β -SrCeCuS ₃ (roasting 1170 K)					
Atom	x	y	Z	Occupancy	U_{eq}
Ce1	0.25501(18)	1/4	0.03815(7)	0.582(5)	0.015(2)
Sr1	0.08931(19)	1/4	0.78499(10)	0.582(5)	0.018(2)
Ce2	0.08931(19)	1/4	0.78499(10)	0.418(5)	0.018(2)
Sr2	0.25501(18)	1/4	0.03815(7)	0.418(5)	0.015(2)
Cu	0.11912(31)	1/4	0.36666(20)	1	0.025(3)
S1	0.0140(5)	1/4	0.59961(29)	1	0.015(3)
S2	0.18081(45)	1/4	0.22153(32)	1	0.016(3)
S3	0.3821(6)	1/4	0.42838(32)	1	0.021(3)



Keywords: complex sulfides, cristal structure, X-ray powder diffraction, Method of vacuum sealed quartz ampoules, rare-earth elements.

Tribological characterisation of MWCNT reinforced Si₃N₄ nanocomposites

Zsuzsanna Koncsik¹, Maria Berkes Maros², Laszlo Kuzsella²
metkzs@uni-miskolc.hu

¹assistant lecturer, University of Miskolc, Hungary, Institute of Materials Science & Technology

²associate professor, University of Miskolc, Hungary, Institute of Materials Science & Technology

Monolithic Si₃N₄ is a good candidate material for many technical applications because its excellent mechanical properties but due the applied sintering additives the remaining glassy phase in grain boundaries degrades the mechanical properties. To improve the mechanical performance of silicon nitride based ceramics nowadays carbon nanotubes as reinforcing nanophase are used.

As carbon nanotubes present exceptional mechanical, thermal and electrical properties in general, there are high expectations also in case of ceramics for improvement of quality. From tribological aspect of view it is expected, that the tribological properties will be more advantageous in case of composites, than in case of monolithic silicon nitride.

In the experimental procedure multiwall carbon nanotube (MWCNT) added silicon nitride ceramic matrix composites have been prepared, with different amount of secondary phase (0, 1, 2 wt%). Pin-on-disc tribological tests were carried out under several loading conditions – changing loading force and sliding rate – at room temperature, without lubricant. The experiments have been carried out using a CETR-UNMT1 multi-functional micro-nano surface tester. The primary goal of the research work is to investigate the effect of composition and test parameters on the tribological behaviour of the investigated silicon nitride based nanocomposites.

In case of the investigated Si₃N₄ based nanocomposites and the applied tribo-systems, the increasing amount of MWCNT as well as the increase of the applied load and sliding rate resulted in an increased wear rate, i.e. decreased wear resistance. However at a certain combination of the loading force and sliding rate – at F = 40N and v = 100 m/s – the wear rate showed a local minimum for all three types of composites. This local minimum for each composition represents the highest wear resistance and enables an optimization of the wear damage processes if choosing the most advantageous combination of loading conditions.

Keywords: *silicon-nitride nanocomposite, carbon nanotube, pin-on-disc test, UNMT-1 micro-nano surface tester*

Enhancing the tribological performance of silicon nitride-graphene nanocomposites by SPS technology

Maros, B. M.¹, Németh, A. K.¹, Károly, Z.², Bódis, E.², Maros, Zs.³,
Tapasztó, O.⁴, Balazsi, K.⁴, Rózsahegyi, P.⁵, Csitkó, Zs.⁵
maria.maros@uni-miskolc.hu

¹University of Miskolc, Institute of Materials Sciences & Technology, Miskolc, H3516, Hungary

²Research Centre for Natural Sciences, Institute of Materials and Environmental Chemistry, H1117, Hungary

³University of Miskolc, Institute of Manufacturing Sciences, Miskolc, H3516, Hungary

⁴Research Centre for Natural Sciences, Institute for Technical Physics and Materials Science, Hungary

⁵Bay Zoltán Nonprofit Ltd. for Applied Research, BAY-LOGI, Miskolc, H3519, Hungary

Silicon nitride is one of the most versatile ceramic materials, widely used as engine parts, ceramic bearings, turbine blades, biomedical parts, cutting tools, insulators, cantilever for AFM, etc. It plays an important role in our age.

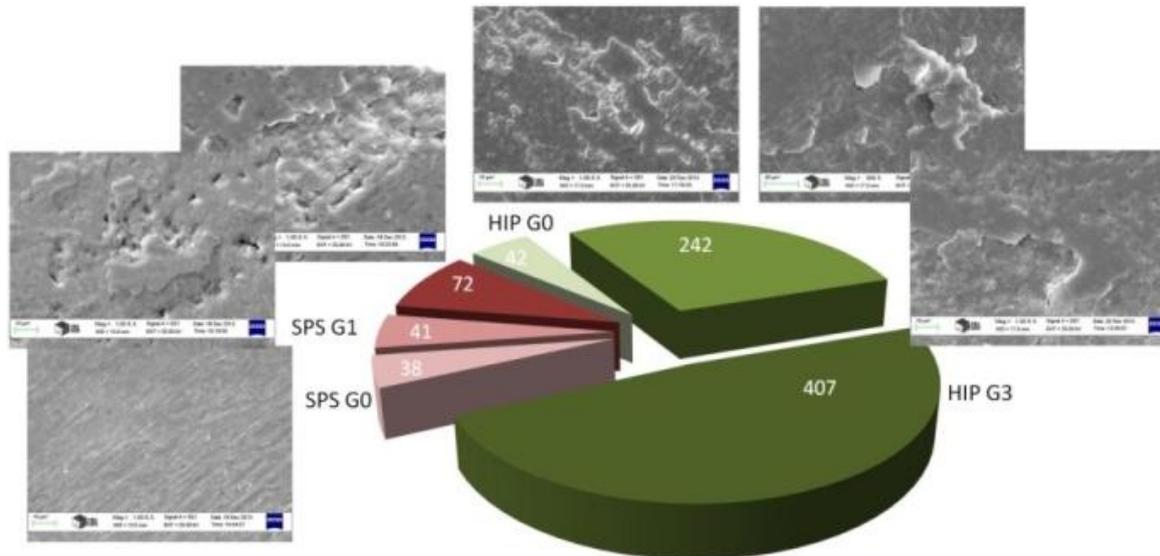
Our focus has put on the silicon nitride products of tribological applications, with special regards of finding cost efficient, environmentally friendly, rapid consolidation techniques. Spark Plasma Sintering (SPS) is such a promising method, gaining today wider and wider application in the ceramic industry. Its advantages are the quick heating rate, extremely short sintering time, providing possibility to avoid undesired microstructural changes like grain growth, GB precipitation of impurities or formation of non-desired new phases. Comparing to the traditional Hot Isostatic Pressing (HIP) the mechanical and physical properties may be significantly improved.

SPS may be utilized for time and cost efficient mass production of novel gradient materials, tailored material structures, various composites and nanocrystalline materials. In production of wear resistant silicon nitride based products the importance of the SPS is growing further on, since it can serve the alpha silicon nitride crystal structure of the ceramic powder, that possess higher hardness than the beta phase developing during a HIP process.

Our research aimed at comparing the microstructure, tribological and mechanical behaviour of HIP and SPS produced silicon nitride nanocomposites, containing different amount – 0, 1 and 3% – of multilayer graphene (MLG), as second phase. We executed pin-on-disc test using an UNMT-1 tribotester applying $F = 40$ N normal load and $v = 200$ mm/s sliding speed at room temperature in dry sliding conditions. The wear performance was characterized by the worn cross section area and friction coefficient. The tribological investigations were completed by the analyses of the wear track morphology and wear mechanisms, determination of the hardness, fracture toughness, elastic modulus, density and phase identification.

The most important observations were as follows: The SPS technology improved the wear resistance of the Si_3N_4 samples for all of the investigated compositions. The effect was more expressed for samples containing MLG additive, in spite of the fact, that with the decrease of the worn cross section the friction coefficient simultaneously increased. Mechanical investigations proved a correlation between hardness and wear rate. The MLG addition did not enhance the wear

performance, while SPS technology was efficient to lower the wear rate by providing several advantageous effect on the microstructure. The paper gives a detailed analysis of the possible microstructural background of the experienced difference in the tribological behaviour of the HIP and SPS specimens. The test results are very promising in point of the attainable increase of the wear resistance provided by the application of the SPS technology.



The worn cross section area of the SPS and HIP specimens with MLG 0% 1% and 3%, A, μm^2

The research work was carried out as part of the TÁMOP-4.2.2/A-11/1-KONV-2012-0029 project in the framework of the New Hungarian Development Plan. The authors also acknowledge the financial support of the National Office for Research and Technology (REG-KM-09-1-2009-0005). Orsolya Tapasztó thanks to Bolyai János Scholarship HAS foundations. Authors thank to Wéber Ferenc from RCNS HAS for sample preparation

Ecology & Economy Fabrication of Metal Nanoparticle Related Materials by Ultrasonic and Microwave Irradiation Methods

Yamato Hayashi, Jun Fukushima, Hirotsugu Takizawa
hayashi@aim.chetohoku.ac.jp

Department of Applied Chemistry, School of Engineering,
Tohoku University, Sendai, 980-8579 Japan

Eco (Ecology & Economy)-fabrication is important in the future manufacturing. There are some elements to achieve this synthesis. When synthesizing, neither waste nor the air pollutant are not generated, and it is safe material is preferable with cheap fabrication device. We developed a new metal nanoparticle related materials synthesis method that achieved in these viewpoints. This new synthesis method is with the ultrasonic and microwave as non-equilibrium reactor and the metal oxide and alcohol based solvent are used for the raw material. Because it is home appliance, the ultrasonic cleaner and the microwave oven are cheap. Ultrasonic irradiation of liquids caused cavitation. Cavitation in a liquid occurs due to the stresses induced in the liquid by the passing of a sound wave through the liquid. These bubbles are now subjected to the stresses induced by the sound waves. The bubbles are filled with vapor and gas, and bubble implosions occur. These implosions are the remarkable part of sonochemical processes. Each of these imploding bubbles can be seen as a high-temperature hot spot having pressures of several hundred atmospheres. Hot spot reaction is considered to represent direct reduction. Microwave irradiation of liquids caused inside and rapid heating, and promoted homogenous chemical reaction. As microwave is electromagnetic field, it affect the electromagnetic properties of the irradiation substance. Therefore, microwave irradiation can expect a special effect or reaction. Starting materials (irradiation materials) are also important. The oxide and alcohol generally are cheap without toxicity. We have synthesized metal nanoparticle related materials by ultrasound and microwave in liquid-solid (alcohol - metal oxide) slurry and controlled morphology of products. Ultrasound and microwave irradiation in liquid-solid process can be expected as chemical non-equilibrium and nonlinear reactors for metal nanoparticle related materials synthesis. The alcohol based solvent and the metal oxide powder are put in the beaker and only irradiated by ultrasound or microwave. The metal oxide simply was reduced into metal and morphology of metal nanoparticles was changed by various conditions. In presentation, we introduce some applications (nanoparticle, nanowire, nanocomposite, etc.) in details.

Keywords: *Ecology, Economy, Ultrasonic, Microwave, liquid-solid, nanoparticle, nanowire, nanocomposite*

Redox Synthesis of Metal/Carbon Nanocomposites

Vladimir Kodolov^{1,2,3}, Vera Trineeva^{1,3,4},
kodol@istu.ru

¹Basic Research – High Educational Centre of Chemical Physics & Mesoscopy, Udmurt Scientific Centre, Ural Division, Russian Academy of Sciences, Izhevsk, Udmurt Republic, Russia

²M.T. Kalashnikov Izhevsk State Technical University, Izhevsk, Udmurt Republic, Russia

³Research Innovation Centre at Izhevsk Electromechanical Plant “KUPOL”, Izhevsk, Udmurt Republic, Russia

⁴Institute of Mechanics, Ural Division, Russian Academy of Sciences, Izhevsk, Udmurt Republic, Russia

The synthesis of nanostructures in nanoreactors of polymeric matrixes is represented the perspective trend for nanochemistry development. Nanoreactors can be compared with specific nanostructures representing limited space regions in which chemical particles orientate creating “transition state” prior to the formation of the desired nanoparticle. Nanoreactors have a definite activity which predetermines the creation of the corresponding product. When nanosized particles are formed in nanoreactors, their shape and dimensions can be the reflection of shape and dimensions of the nanoreactor. The investigation of redox synthesis of Metal/Carbon nanocomposites in nanoreactors of polymeric matrixes is realized in three stages: 1) The computational designing of nanoreactors filled by metal containing phase and quantum chemical modeling of processes within nanoreactors. 2) The experimental designing and nanoreactors filling by metal containing phase with using two methods (the mixing of salt solution with the solution of functional polymer, for example, polyvinyl alcohol; or the common degeneration of polymeric phase with metal containing phase). 3) The properly redox synthesis of metal/carbon nanocomposites in nanoreactors of polymeric matrixes at narrow temperature intervals.

The method of metal/carbon nanocomposite synthesis applied has the following advantages: 1) The perspectives of this investigation are looked through in an opportunity of thin regulation of processes and the entering of corrective amendments during processes. 2) Wide application of independent modern experimental and theoretical analysis methods to control the technological process. 3) Technology developed allows synthesizing a wide range of metal/carbon nanocomposites depending on the process conditions. 4) Process does not require the use of inert or reduction atmospheres and specially prepared catalysts. 5) Method of obtaining metal/carbon nanocomposites allows applying secondary raw materials. In this investigation the possibilities of developing new ideas about self-organization processes during redox synthesis within nanoreactors of polymeric matrixes as well as about nanostructures and nanosystems are discussed on the example of metal/carbon nanocomposites. It is proposed to consider the obtaining of metal/carbon nanocomposites in nanoreactors of polymeric matrixes as self-organization process similar to the formation of ordered phases. The perspectives of this investigation are looked through in an opportunity of thin regulation of processes and the entering of corrective amendments during processes

f

SESSION 13

Phase Diagram as a Tool of Materials Science

Microstructures and properties of thermoelectric silicides

Stéphane Gorsse, Solange Vivès, Philippe Bellanger
gorsse@icmcb-bordeaux.cnrs.fr

Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS), Pessac 33608, France

Ideally, thermoelectric materials should be thermal insulators and electrical conductors with large Seebeck coefficients. This is a quite antagonist combination of properties. In this presentation, we will show that metallurgical concepts and phase diagrams can provide design guidance to change the properties. The distinguishing feature of metallurgy is to act at the level of the microstructure. Many materials properties are controlled by the nature of the interactions between the microstructure and the underlying mechanism, for example phonons in the case of thermal conductivity. Therefore, generating and tailoring the nano/microstructure, such as the grain size and morphology, the texture, and the precipitate distribution is one of the main degree of freedom used by the metallurgist to tune the properties, study the behavior of materials, and improve their performance. We will describe two examples: the first concerns a modelling and combinatorial approach applied to quantify the individual effect arising from the nano/microstructure on the lattice thermal conductivity of nanostructured $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ alloys, and the second is related to the crystallographic texture control of higher manganese silicide.

Keywords: *microstructure, metallurgy, thermodynamic, thermoelectrics.*

Phase relationships and microstructure in Higher Manganese Silicide based alloys

Solange Vivès, Stéphane Gorsse
gorsse@icmcb-bordeaux.cnrs.fr

Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS), Pessac 33608, France

Higher Manganese Silicide (HMS) is considered as an attractive p-type thermoelectric material compatible with industrialization in large volume (low cost production processes, abundant materials) and the rules of hygiene, health and environment. In order to gain some design guidance to further improve the thermoelectric performance of HMS through alloying and the control of its microstructure, it is of paramount importance to have a better understanding of the binary Mn-Si and selected ternary Mn-Si-X phase diagrams since little is known about the thermodynamic of these systems. Among the important discrepancies and questions arising from the literature, we can cite the possible existence of the homogeneity range for the HMS compound, the formation mechanism of intra-granular MnSi striations during solidification, and the solubility limits of the HMS phase in promising ternary systems. In this work, we have investigated the HMS phase boundaries Mn-Si and ternary Mn-Si-X systems selected for their potential interest as thermoelectrics. Our approach involves the use of diffusion couples in addition to more classical experiments. Our results provide new insights into the phase relationships in Mn-Si-based systems and clues regarding the microstructure genesis occurring during solidification, which can be used to suggest strategies for enhancing the thermoelectric performance of HMS.

Keywords: *Higher Manganese Silicide, phase diagram, diffusion couple, microstructure, thermoelectric*

4D Space Models of Quaternary Systems for the Phase Diagrams Graphics Correction

Vasily Lutsyk^{1,2}, Anna Zelenaya¹
vluts@ipms.bsnet.ru

¹Institute of Physical Materials Science SB RAS, Ulan-Ude 670047, Russia
²Buryat State University, Ulan-Ude 670000, Russia

Space model contain the information about any geometrical element of T-x-y-z diagram. The nonplanar tie-lines method for the determination of invariant points using the matrix transformation of concentration coordinates was elaborated by means of 4D computer models [1]. It's based on the construction of three two-dimensional vertical sections. Two first sections (not belonging to one plane) permit to define the point on tie-line at the temperature of quaternary eutectic. The third vertical section is constructed through the found point and the nearest tetrahedron's vertex till the intersection with the section of horizontal hyperplane. This section should contain the required point of quaternary eutectic. This method permitted to find the inaccuracies of experimentally constructed isopleths in some salt systems.

Space models permits to avoid the errors at the experimental data interpretation. They are used to correct the fluoride compositions for the spent nuclear fuel reprocessing [2] and for the molten salt reactor of Generation IV [3]. E. g., a mistake in vertical section of system LiF-BaF₂-MgF₂-ZrF₄ was found [2]. Authors firstly determined a ternary eutectic in system LiF-BaF₂-MgF₂, and then assumed that the segment connected it with the opposite tetrahedron vertex contains the quaternary eutectic point. Whereas the model of phase diagram shows that really the point of quaternary eutectic wasn't found [4] and the arrangement of ternary and quaternary eutectics on one tie-line is the particular case of phase diagram structure.

Keywords: *phase diagram, quaternary system, computer model, generation IV reactor*

Acknowledgements. Authors are grateful for the support to the Russian Foundation for Basic Research (project 14-08-00453).

[1.]Lutsyk V., Zelenaya A. Solid State Sciences. 2012. Vol. 14, P. 1604-1608.

[2.]Li G., Takagi R., Kawamura K. Denki Kagaku. 1991. Vol. 59, P. 800-801.

[3.]Lutsyk V., Zelenaya A., YaZhou Dai. Advanced Materials Research. 2013. Vol. 704. P. 349-352.

[4.]Lutsyk V.I. ECS Proceed. 2002. Vol. PV2002-19. P. 386-398.

Topological Correction of Multicomponent System Polyhedration

Vasily Lutsyk^{1,2}, Vera Vorob'eva¹
vluts@ipms.bsnet.ru

¹Institute of Physical Materials Science SB RAS, Ulan-Ude 670047, Russia

²Buryat State University, Ulan-Ude 670000, Russia

Novel algorithm for quaternary systems (additive and reciprocal) polyhedration has been elaborated and special topological formulas have been derived (Lutsyk V.I., Vorob'eva V.P. "Algorithm for Topological Correction of Simplexes Lists with Different Dimension for Multicomponent Systems Polyhedration" & "Inner Diagonals Enquiry for Polyhedration of Reciprocal Systems by Means of Topological Correction Algorithm of Simplexes Lists with Different Dimension"; to be published by Russian Journal of Inorganic Chemistry in 2014).

Initial polyhedron of multicomponent system is represented as a graph. The numbers of geometric elements for the triangulated complex of quaternary system has been interconnected: vertexes, links between them (graph edges), planes (2D simplexes) and tetrahedrons (3D simplexes). All known links in boundary systems are analyzed and the links inside the polyhedron are enquired. Firstly all possible lists of tetrahedrons and inner planes are formed. Then the inner elements (diagonals and planes) are chosen, which fits the real variant of polyhedration.

Algorithm helps to control all stages of polyhedration process and takes into account the competition of inner diagonals. It has been used to investigate the molten salt systems for the reactor of Generation IV. Besides the lowest melting point another criterion is the same important for the salt fuel: a concentration of fissile material. Fluoride systems have been described as one of the possible fuels for molten salt reactor application. Chloride systems have more high pressure of vapor and more low thermodynamic stability, but they are less aggressive for the reactor materials and their melting points are lower. As a result, the reciprocal fluoride-chloride systems have the more perspectives. To optimize the molten salt fuel parameters the computer models of their phase diagrams are to be built. To ensure reliable exploitation of new generation reactor, exhaustive information is to be used about the chemical processes and equilibrium in the fluoride-chloride reciprocal systems.

Keywords: *triangulation, multicomponent system, molten salts, IV generation reactor.*

Aknowledgements. Authors are grateful for the support to the Russian Foundation for Basic Research (project 14-08-00453).

Calphad modeling of the Ni-Sn-Ti system

A. Berche, J.C. Tédénac, P. Jund
tedenac@univ-montp2.fr

ICGM-Université Montpellier II, UMR-CNRS 5253, Pl. E. Bataillon CC1506
34095 Montpellier, France

Among the potential semiconducting materials for thermoelectricity applications, Half-Heusler phases such as NiTiSn show interesting properties. The knowledge of thermodynamic properties and phase stabilities is necessary for the optimization of the thermoelectric properties and to determine the more appropriate synthesis way. This is why the Calphad assessment of the ternary system is performed.

After a careful analysis of the constitutive binary systems, the parameters of some binary phases have been slightly modified.

This system is characterized by the existence of some ternary intermetallic compounds and the ternary extension of binary ones.

Moreover, the continuous solubility region between Ni₂TiSn and NiTi at high temperature induces that these phases have to be modeled as a single phase. Such description is supported by the previous DFT calculations.

According to the Calphad procedure, the solubility of ternary element in the binary phases and thermal analysis measurements are taken into consideration to obtain a global description of the Ni-Ti-Sn system.

Keywords: *intermetallics, phase stabilities, phase equilibria, Calphad.*

Calphad assessment of Cr-Mn-Si

Alexandre Berche
alexandre.berche@gmail.com

Institut Charles Gerhardt, MESO

For thermoelectric applications, Higher Manganese Silicides (HMS) MnSi_x (with x around 1.75) exhibit interesting figures-of-merit at intermediate temperatures (573K to 873K). Moreover it appears that the figure-of-merit can be improved by chromium doping. The optimization of the elaboration of such alloys needs the knowledge of the ternary Cr-Mn-Si system and of its constitutive binaries. First principles calculations are performed to clarify the enthalpies of formation of the intermetallic phases. Especially the enthalpies of formation of various metastable phases and the enthalpy of mixing in possible solid solutions are calculated using DFT. On the basis of these new data, a thermodynamic description of the Gibbs energy of the phases is performed using the Calphad method.

Bifurcation and “Self-Organization” of a System

Gulshat Balakaeva¹, Mailybi Aldabergenov
e-mail: aldabergenov_m@mail.ru

Al-Farabi Kazakh National University, Al-Farabi ave.71, Almaty 050038, Kazakhstan
1K.I.Satpaev Kazakh National Technical University, Satpaev ave.22, Almaty 050013,
Kazakhstan

Some of the characteristic features of non-equilibrium systems are the presence of fluctuations, instability, breakage of the symmetry, rising of coherence, correlation, “selforganization”, etc. An unpredictable states of the system appear in the points of bifurcation.

The authors have proposed a new concept “The Gibbs function normalized to the total number of electrons”. Its physical meaning is to define the chemical bond in terms of a collective effect of electron-nuclear interaction. Basically, the density of the energy of formation per one electron is determined. During the bonds formation “The Gibbs function normalized to the total number of electrons” adequately reacts to the all changes in the structure of the compound. Also it is possible to carry out triangulation.

On the basis of this concept, the triangulation of solidphase CaO-SiO₂-H₂O system was carried out. The possibility of determining both the points of bifurcation and the processes of the system self-organizations was shown. The main feature of the system’s triangulation is the determination of components which can form only eutectic compositions. Components of a single phase unit block don’t interact with each other, but components of the different phase unit blocks do. Therefore, according to the method that was explained above, the phase transition of the system components in the various reactions can be determined. Also the all paths of the components bifurcation as well as the existence of the new compounds can be predicted.

It was found that famous Radischev’s conversion points occur to be the same as bifurcation points. During the dehydration and polycondensation reactions asymmetric bifurcation tend to happen. Also it was shown that “Self-organization” of an open system occurs on the basis of exchange reactions through the synergic processes. By the means of triangulation of the systems all these processes on certain chemical reactions can be described.

Keywords: *non-equilibrium thermodynamic, bifurcation, self-organization.*

Phase Equilibria in the Ti-Co-Sn System at Crystallization

Iuliia Fartushna¹, Marina Bulanova¹, Jean-Claude Tedenac²
juliefart@mail.ru

¹ Institute for Problems of Materials Science, Krzhizhanovsky 3, 03680 Kiev, Ukraine

² Université Montpellier II, Place E. Bataillon , 34095 Montpellier Cedex 5, France

Information on phase equilibria in the Ti-Co-Sn system concerns partial isothermal sections at 870 and 1070 K, and thermodynamic calculation. Two ternary compounds – TiCo_2Sn (τ_1) (structure type MnCu_2Al , Fm-3m, $a = 6.067 \text{ \AA}$) and TiCoSn (τ_2) (structure type MgAgAs , F-43m, $a = 6.003 \text{ \AA}$) were reported earlier. These compounds are full-Heusler and half-Heusler phases, respectively. No experimental data on crystallization of the alloys are available. Thus, the goal of the present research was to study phase equilibria in the Ti-Co-Sn system below 50 at. % Sn at crystallization.

Phase equilibria in the Ti-Co-Sn system were studied by the methods of DTA, X-ray diffraction, SEM and electron probe microanalysis. The partial liquidus and solidus projections and the melting diagram (liquidus + solidus) were constructed. It was shown that the ternary compound τ_1 melts congruently above 1450°C and coexists with majority the phases based on the binary compounds in the concentration interval studied. The ternary compound τ_2 does not exist at solidus temperature. The full-Heusler phase (τ_1) has a significant homogeneity region, which is not less than 15 at.% by tin and about 9 at.% by nickel / titanium. At decreasing tin concentration the width of homogeneity region of τ_1 by nickel / titanium decreases.

Among the binary compounds TiCo and Ti_5Sn_3 have the widest homogeneity regions. TiCo phase dissolves ~10 at.% Sn. Solubility of Co in Ti_5Sn_3 at solidus temperature was established as 11 at.%. We found that the Ti_5Sn_3 based solid solution is the interstitial phase, which orders at composition Ti_5CoSn_3 with the Hf_5CuSn_3 structure type (ordered derivative of Ti_5Ga_4 , *hP18-P6₃/mcm*). The Co atoms occupy [Ti6] octahedral interstices (Wyckoff position 2b) up to the composition Ti_5CoSn_3 . Solubility of Co in Ti_6Sn_5 was established as 5 at.%. Solubility of Co in Ti_2Sn was established as not less than 5 at.%. TiCo_2 dissolves up to 4 at.% Sn. Ti_3Sn , Ti_2Co , TiCo_{2-x} , TiCo_3 , $\beta\text{Co}_3\text{Sn}_2$ and CoSn have narrow homogeneity regions, and dissolve about 1 at.% of third component.

The liquidus surface is characterized by the fields of primary crystallization of phases on the basis of βTi , Ti_3Sn , Ti_2Sn , Ti_5CoSn_3 , Ti_6Sn_5 , Ti_2Co , TiCo , TiCo_{2-x} , TiCo_2 , TiCo_3 , $\beta\text{Co}_3\text{Sn}_2$, (αCo) and τ_1 .

Twelve three-phase fields are present in the solidus surface: (βTi)+(Ti₂Co)+(Ti₃Sn), (Ti₃Sn)+(Ti₂Co)+(TiCo), (Ti₂Sn)+(Ti₃Sn)+(Ti₅CoSn₃), (Ti₃Sn)+(Ti₅CoSn₃)+(TiCo), (Ti₅CoSn₃)+(TiCo)+ τ_1 , (Ti₅CoSn₃)+(Ti₆Sn₅)+ τ_1 , (TiCo)+ τ_1 +(TiCo_{2-x}), τ_1 +(TiCo_{2-x})+(TiCo₂), τ_1 +(TiCo₂)+(αCo), (TiCo₂)+(TiCo₃)+(αCo), τ_1 +(βCo₃Sn₂)+(αCo), τ_1 +(βCo₃Sn₂)+(CoSn).

Keywords: phase diagram, liquidus surface, solidus surface, melting diagram

Growth and Characterisation of New Borate Based Crystal Fibers by the Micro Pulling Down Technique

F. Assi^{1,2}, M. Cochez*^{1,2}, M. Ferriol^{1,2}, M. Aillerie^{1,2}, G. Maxwell³
* marianne.cochez@univ-lorraine.fr

¹ University of Lorraine, LMOPS, E.A. 4423, F-57070, Metz, France

² Supélec, LMOPS, E.A. 4423, F-57070, Metz, France

³ Shasta Crystals Inc., Anderson, California, U.S.A.

Compact all solid-state lasers emitting in the blue and ultraviolet range are more and more required for numerous applications such as data storage, materials processing, photolithography, micromachining, sensors for the detection of gaseous pollutants, in biology or medicine. In this frame, single crystals allowing the generation of a blue/UV radiation by frequency conversion of an infrared one are promising materials. Crystals of the borate family are good candidates such as Bi₂ZnB₂O₇ (BZBO) chemically stable and not hygroscopic. Bulk single crystals were recently grown for the first time by Czochralski and Kyropoulos techniques [1-5].

On the other hand, a big interest has arisen for fiber crystal growth techniques such as the micropulling down (μ -PD) due to its unequalled specifications: high axial temperature gradients allowing high pulling rates, high length/diameter aspect ratio favorable to light propagation, high crystal quality,...

Several BZBO crystal fibers were pulled and characterized. All were transparent with a more or less pronounced yellow-orange/red color. The origin of this color is ascribed to the presence of Bi-rich disordered or glassy domains. The presence of these disordered domains may be caused by the contamination of Pt crucible.

In order to obtain colorless fibers, the growth of BZBO was studied by μ -PD technique using a gold crucible and also by LHPG (Laser-heated pedestal growth) technique taking advantage of the absence of crucible avoiding any contamination.

Keywords: borate crystals, μ -PD, crystal fibers, LHPG

[1] N. Li, P. Fu, Y. Wu, J. Zhang, J. Cryst. Growth, 311, 3476 (2009)

[2] F. Li, S. Pan, X. Hou, J. Yao, Cryst. Growth Des., 9, 4091 (2009)

[3] F. Li, X. Hou, S. Pan and X. Wang, Chem. Mater., 21, 2846 (2009)

[4] F. Li, S. Pan, X. Hou, Z. Zhou, J. Cryst. Growth, 312, 2383 (2010)

[5] F. Li, S. Pan, J. Cryst. Growth, 318, 629 (2011)

LaBGeO₅ Single Crystal Fibers

Farah Assi^{1,2}, Michel Ferriol^{1,2}, Marianne Cochez^{1,2}, Michel Aillerie^{1,2}, Gisèle Maxwell³
farah.assi@univ-lorraine.fr

¹ University of Lorraine, LMOPS, E.A. 4423, F-57070, Metz, France

² Supélec, LMOPS, E.A. 4423, F-57070, Metz, France

³ Shasta Crystals Inc., San Francisco, California, U.S.A

The growing interest in compact all-solid state laser sources based on non-linear optical crystals emitting in the ultraviolet range is explained by their numerous applications such as photolithography, marking, micromachining, cutting or surgery. The only way to generate an ultraviolet laser light from a crystal is by frequency conversion of a near-infrared source. In these conditions, the research works focus towards borate crystals as new non-linear optical materials due to their performance, transparency and resistance to laser damage. A particular interest is directed to the LaBGeO₅ compound (LBGO), which is chemically stable and non-hygroscopic.

Nowadays, few works were performed on LBGO crystal growth by using the Czochralski method (Belokoneva et al. [1]). The results of differential thermal analysis shows that this crystal is congruently melting ($T^{\circ} = 1150\text{-}1200^{\circ}\text{C}$) [1, 2]. However, the growth procedure is complicated due to high viscosity of the melt and violent evaporation of B₂O₃ during pulling [3].

The recent work of Miyazawa [4] using also Czochralski method shows that the LBGO single crystals grown with the pulling rate of 0.5 mm/h under O₂-flowing are colorless and transparent. The crystal grown with N₂-flowing looked cloudy or opaque due to the presence of cracks.

The direct growth of LBGO fibers from the melt by micro-pulling down method is impossible because of its excessive viscosity. Therefore, it is necessary to find a flux to reduce viscosity and provide crystals with good quality and usable dimensions. It was shown that fluoride ions break extended -O-B-O- chains and then reduces viscosity [5]. So, a LiF flux was considered and the LBGO-LiF phase diagram was studied.

For the same purpose, the isoplethal section La₂O₃- LaBGeO₅ in the La₂O₃-B₂O₃-GeO₂ ternary system is also investigated to examine the possibility of "self-flux".

The growth of LBGO using LiF flux was made. High volatility of LiF coupled with important migration of the melt on the crucible walls due to surface tension phenomena did not allow to grow good fibers. To solve this problem LiF is will be replaced by another fluoride-based flux presently under investigation.

Keywords: borates, LBGO fibers, micro-pulling down (μ -PD), phase diagram

References

- [1] E.L. Belokonova, B.V. Mill, A. V. Bustashin, A. A. Kaminskii, Izv. Akad. Nauk. SSSR, Ser. Neorg. Mater. 27, 556 (1991).
- [2] V.N. Sigaev, S.Yu. Stevanovich, P.D. Sarkisov, E.V. Lopatina, « Stillwellite galss- ceramics with ferroelectric properties », Materials science and engineering B32 (1995) 17-23.
- [3] C.T.Chen, Development of new nonlinear optical crystals in the borate series (Harwood Acad, Pub., Switzerland,1993).
- [4] S.Miyazawa, S. Ichikawa, Y.Liu, S. Ji, T. Matsuoka, Phys. Status Solidi A 208, No. 5, 1195–1198 (2011).
- [5] D. Elwell, H.J. Scheel, Crystal Growth from High Temperature Solutions, Academic Press, London, 1975.

Experimental investigation and thermodynamic modeling of the ZrO₂-MgO-MnO-Mn₂O₃ system

Dmytro Pavlyuchkov, Galina Savinykh and Olga Fabrichnaya
d.pavlyuchkov@gmail.com

Technical University of Freiberg, Institute of Materials Science, D-09599 Freiberg, Germany

Magnesia partially stabilized ZrO₂ (Mg-PSZ) was proposed as a reinforced component of the TRIP-matrix composite [1]. The aim of our investigation is a development of thermodynamic database for simulation of interface reactions between steel and ceramic material. Information about phase relations in the Zr-Mg-Mn-O system is important to understand interaction between Mg-PSZ and Mn being one of the alloying component of the austenitic steel. Manganese oxidizes and forms MnO at relatively low partial pressure of oxygen relevant to the processing conditions of TRIP steel composite. In the present work the focus is on experimental study of phase equilibria in the system Zr-Mg-Mn-O as well as corresponding thermodynamic modelling.

The ZrO₂-MgO phase diagram was recently reassessed using two-sublattice ionic models for the ZrO₂ based solutions [2] and accepted in our present work.

Phase equilibria in the Zr-Mn-O system were already modelled for air conditions [3]. The phase diagram of ZrO₂-MnO system was experimentally constructed in Ref. [4]. However phase relations below 1550°C and the invariant reactions involving structural transformations in the ZrO₂ based solid solutions were not investigated so far.

Samples were prepared by co-precipitation method from aqueous solutions and heat treated at selected temperature in inert atmosphere and in air. Microstructural investigations were carried out using X-ray phase analysis and SEM/EDX technic. Temperatures of transformations were determined by DTA.

Using experimental data obtained in the present work and literature a thermodynamic dataset of the ZrO₂-MnO system was developed by the Calphad approach. In order to derive the ZrO₂-MgO-MnO-Mn₂O₃ dataset our data were combined with those presented in Ref. [3]. For these reasons the solid solutions of the ZrO₂ polytypes were described using ionic model assuming that Mg⁺², Mn²⁺ and Mn³⁺ ions substitute for Zr⁴⁺ on its sublattice. Ionic liquid model was used to describe the liquid phase.

Keywords: ZrO₂, phase diagram, CALPHAD

References:

- [1] H. Biermann, U. Martin, C.G. Aneziris, A. Kolbe, A. Müller, M. Herrmann, 2009, *Microstructure and Compression Strength of Novel TRIP-Steel/Mg-PSZ Composites*, *Adv. Eng. Mater.* 11, pp 1000-1006
- [2] D. Pavlyuchkov, G. Savinykh, O. Fabrichnaya, 2013, *Experimental investigation and thermodynamic modeling of the ZrO₂-MgO system*, *Adv. Eng. Mater.* 15, pp. 618-626
- [3] M. Chen, B. Hallstedt, L.J. Gauckler, 2005, *Thermodynamic modeling of phase equilibria in the Mn-Y-Zr-O system*, *Solid State Ionics*. 176, pp. 1457-1464
- [4] R.L. Shultz, A. Muan. 1971, *Phase Equilibria in the System MnO-FeO-ZrO₂-SiO₂*, *J. Am. Ceram. Soc.* 54, pp. 504-510

Thermodynamics of Ti-Ni-based shape memory alloys extended by Cu-addition

E. Povoden-Karadeniz¹, P. Lang², D.C. Cirstea³, T. Wojcik⁴, E. Kozeschnik^{1,4}
erwin.povoden-karadeniz@tuwien.ac.at

¹Christian Doppler Laboratory for Early Stages of Precipitation, Institute of Materials Science and Technology, Vienna University of Technology, Favoritenstraße 9-11, 1040 Vienna, Austria.

²Department of Materials Science and Metallurgy, University of Cambridge, Charles Babbage Road 27, Cambridge, CB3 0FS, UK

³National Institute for Research and Development in Electrical Engineering INC DIE ICPE-CA, Advanced Materials Department, Splaiul Unirii, nr. 313, sector 3, Bucharest, Romania.

⁴Institute of Materials Science and Technology, Vienna University of Technology, Favoritenstraße 9-11, 1040 Vienna, Austria.

Ti-50Ni to Ti-55Ni (at%) can be termed as the pioneer of shape memory alloys (SMA). Metastable precipitates play an important role for the start temperature of the martensitic transformation, which is a crucial property for the shape memory effect. CALPHAD descriptions of these metastable intermetallic phases are presented. The thermodynamics of Ti_3Ni_4 and Ti_2Ni_3 are described with experimental solvus data and molar enthalpies at 0 K from new first-principles analysis. New thermodynamic data suggest that the thermodynamic description of the DO_{24} -ordered $TiNi_3$ and the Ti-Ni alloy phase as well as B2-ordered austenite and B19' martensite phases also need to be re-assessed. These modifications have important consequences on the martensite formation. Efforts for increasing the martensite start temperature include replacement of a part of Ni atoms by Cu [1]. The influence of Cu-addition to Ti-Ni SMA on T_0 -temperatures on the diffusionless austenite-martensite transformation and on the occurrence of metastable phases is evaluated by computational thermodynamics using our thermodynamic Ti-Ni-database extended by Cu.

[1] T. Corycka, J. Van Humbeeck, Characterisation of a NiTiCu shape memory alloy produced by powder technology, JAMME 17 (2006) 65-68.

f

SESSION 14

Polymer Derived Ceramics

Investigation of alumina samples cast from concentrated polymer suspensions

Lilla Angyal¹, Zsuzsanna Karácsony², Alfréd Kállay-Menyhárd¹, György Bánhegyi²
zsuzsa.karacsony@bayzoltan.hu

¹Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, 1111 Budapest, Műegyetem rakpart 3., building H, Hungary

²Bay Zoltán Nonprofit Ltd. for Applied Research, 1116 Budapest Fehérvári út 130., Hungary

Various ceramic processing technologies utilize concentrated ceramic suspensions to produce shaped ceramic end products (e.g. slip casting, tape casting, gel casting, low pressure injection molding etc.). In these technologies the “green body” is obtained by drying the suspension followed by debinding (thermal decomposition of the polymer component) and finally by sintering of the “brown body”. The advantage of these techniques over powder injection molding (PIM) is that they usually require less organic binder, thus they are cheaper and more environmentally friendly. Suspensions usually exhibit lower viscosity than concentrated mineral filled melts, so the shaping is easier, but it has to be noted that the cycle time is slower than in PIM due to the drying time which can be accelerated by heating. One of the most frequently used technical ceramics processed into shaped products is alumina (with various purity levels: 99.5%, 99.7% or better – the higher the purity the lower the conductivity and the better the heat and chemical resistance).

In this research we investigated a special system containing alumina filler and ethylene-ethyl acrylate (EEA) solutions as liquid phase. As EEA dissolves in water only under high pH conditions, we have tried to use both NaOH and concentrated aqueous ammonia solution to produce the polymer solution. It has to be noted, that not all EEA grades dissolve in water even under such conditions, therefore first we had to select the proper polymer grade. When preparing the samples we varied the following parameters: NaOH or NH₄OH for dissolving the polymer, the concentration of the polymer solution (the relative amount of the filler and of the liquid phase was kept constant), and the composition of the filler: in some samples we replaced a part of Al₂O₃ by Al(OH)₃ (ATH). It is expected that in the case of ATH the greater concentration of surface Al-OH groups as compared to alumina (where such groups are formed only by partial hydration) produces stronger physical network. The potential advantage of using ammonia instead of NaOH is that the ammonium salts decompose and evaporate at high temperature, not causing further contamination in the pure Al₂O₃ product to be prepared. It is more important in the case of high purity alumina samples.

The thermal decomposition process was studied by TGA/DTA in argon and in air, the debinding and sintering processes were studied in ventilated ovens. The rheological properties of the EEA solutions and the suspensions made of them were studied by rotation and oscillation rheometry as a function of frequency, amplitude and shear rate respectively. Nonlinearities in terms of frequency and oscillation amplitude are observed. The density of the sintered bodies is studied by Archimedean balance, which also allows the assessment of closed porosity. Open porosity is estimated by mercury porosimetry. The morphology of the sintered bodies is studied by optical and by scanning electron microscopy. The mechanical properties are studied by 3-point bending and the flexural strength values are correlated with the bulk density values measured earlier. These studies offer good chance to optimize a large scale technology based on these principles.

Keywords: slip casting, alumina, ethylene-ethyl acrylate, slurry

Influence of Carbon Enrichment on Electrical Conductivity and Processing of Polycarbosilane Derived Ceramic.

Federico Dalcanale^{1,2}, Jonas Grossenbacher³, Gurdial Blugan¹, Maurizio Gullo³,
Alessandro Lauria², Jürgen Brugger³, Hendrik Tevaearai⁴, Thomas Graule¹,
Markus Niederberger², Jakob Kuebler¹

federico.dalcanale@empa.ch

¹Empa, Laboratory for High Performance Ceramics, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, Duebendorf, Switzerland

²Laboratory for Multifunctional Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland

³Microsystems Laboratory, EPFL, Station 17, CH-1015 Lausanne, Switzerland

⁴Clinic for Cardiovascular Surgery, Inselspital Berne, Berne University Hospital and University of Berne, Berne, Switzerland

Among all the ceramics classes, Polymer Derived Ceramics (PDC) have the unique property to be produced from a liquid polymeric precursor. This innovative route overcomes the limits of traditional powder technology (e.g. shape complexity, porosity, microfabrication) and makes PDC a highly promising material for micro electrical mechanical systems (MEMS) production. In addition, the final ceramic properties (e.g. electrical, mechanical, thermal resistance) can also be tuned modifying the polymer chemistry or adding suitable fillers. Despite these advantages, the fabrication of a bulk crack free sample presents many difficulties due to the consistent linear shrinkage and gas release during pyrolysis. Few examples of integer samples produced via liquid route are reported in literature and mainly for polysiloxanes and polysilazanes.

We will present the effect of carbon enrichment of allylhydridopolycarbosilane SMP10[®] with divinylbenzene (DVB). 14 mm diameter disc shaped samples were produced via liquid route and cured without applying external pressure. Raman analysis after pyrolysis at 800-1400 °C reveals that the segregation process of the excess carbon is concentration and temperature dependent. This can already lead to the formation of disordered carbon clusters at 800°C if sufficient DVB is added. The effect of these two parameters on the electrical conductivity brings to an improvement of 7 orders of magnitude. Among the analyzed compositions, the addition of an optimum amount of DVB has been found. Carbon was preserved in the microstructure during pyrolysis and the ceramic yield increased from 77.5 to 80.5 wt. %. The electrical conductivity increased from 10⁻⁶ to 1 S/cm depending on the annealing temperature. Furthermore, the ceramic samples obtained with this composition were found to be in many cases crack free or with minimal cracks in contrast with the behavior of pure SMP10.

Keywords: *Polymer derived ceramics, divinylbenzene, electrical conductivity, polycarbosilane*

Manufacturing of Polymer-Derived Ceramics With Negative Thermal Expansion Materials As Fillers

A. Fedorova¹, M. Scheffler¹

¹ Institute of Materials and Joining Technology (IWF), Otto-von-Guericke University Magdeburg, D-39106 Magdeburg, Germany

Over the past decades the group of materials with negative thermal expansion (NTE materials) has attained growing interest. The dominant system among the NTE-materials is the lithium-aluminosilicate glass-ceramics ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$) system (LAS), which forms during controlled thermal management of glasses during the transformation into a glass-ceramic. Its widely studied representative with the lowest value of CTE is β -Eucryptite. Due to an overall negative bulk thermal expansion it provides, among others, high thermal stability and high thermal shock resistance when embedded in a matrix, and technical applications have been realized, e. g. as support for telescope mirrors or as domestic cookware.

In the present study β -Eucryptite was prepared by a solid-state synthesis procedure. It was mixed with a methyl silicon resin (60-40 vol.-% resin, 40-60 vol.-% β -Eucryptite) and test specimens were produced by warm-pressing, which caused the simultaneous cross-linking. Pyrolysis was performed in different atmospheres at temperatures of up to 1100 °C. X-Ray diffraction, simultaneous thermal analysis, dilatometry and porosity measurements were carried out to study sintering characteristics, phase transformation and thermal expansion behavior of the sintered samples. This paper discusses material properties, gives some insights into specific materials problems and processes, occurring during the synthesis and highlights potential applications.

Keywords: *polymer-derived ceramics, NTE-material, manufacturing of ceramics*

Basalt Fiber Reinforced SiOC-Matrix Composites for Intermediate Service Temperatures

Patrick Weichand¹, Rainer Gadow¹
patrick.weichand@ifkb.uni-stuttgart.de

¹Institute for Manufacturing Technologies of Ceramic Components and Composites, University of Stuttgart, Stuttgart D-70569, Germany

Polymer Matrix Composites (PMC) are widely used in lightweight applications. The manufacturing technologies are fully developed and raw materials are cheap. The limiting factors of these reinforced polymers are the maximum useable service temperature and poor tribological properties.

Ceramic Matrix Composites (CMC) are suitable for service temperatures well above 1000 °C. These composites are composed of ceramic matrices combined with ceramic fibers based on alumina or silicon carbide. This class of composites is handicapped by the high cost of processing and raw materials and therefore only attractive for applications in astronautics and military aviation. Composite materials, bridging the gap between PMC and CMC, are manufactured by the use of polysiloxanes and basalt fibers. Such competitive free formable Hybrid-Composite are capable for service temperatures up to 600 °C in oxidative atmosphere. In order to qualify the material for series applications, manufacturing technologies like Resin Transfer Moulding (RTM), filament winding or pressing techniques are employed.

Beside the improved thermal resistivity in comparison to reinforced polymers and light metals, a major benefit of the SiOC composites is investigated in the field of friction materials. The excellent properties in wear resistance and an adjustable coefficient of friction make it an interesting alternative for CFC and CMC.

Keywords: *Hybrid Composites, CMC, Basalt fiber, SiOC, Siloxane, tribological testing*

Hierarchical Carbon Structures from Preceramic Polymers: Carbon Nanotubes Covered Carbon Fibers

Niko Mantzel, Eric Reissig, Stefan Rannabauer, Michael Scheffler
niko.mantzel@ovgu.de

Otto-von-Guericke University Magdeburg, Institute of Materials and Joining Technology
D-39106 Magdeburg, Germany

Lightweight construction is an important issue in current research and development due to a steady decrease in resources availability. One of the lightweight strategies makes use of carbon nanofibers due to their excellent mechanical and thermal properties. To enable these properties, they often are processed into a composite with a polymer matrix (carbon-fiber reinforced polymer; CFRP) or a ceramics matrix (ceramic matrix composite; CMC).

The fiber/matrix bond in these composites is an important issue to produce a stable and high-strength material. To improve these bonds, carbon fibers were overgrown with carbon nanotubes (CNTs) by two different processes: In the first process, the carbon fibers were coated with a catalyst precursor. During the thermal treatment in argon atmosphere, the catalyst precursor was transformed into the catalyst and a hydrocarbon-releasing precursor placed beneath the carbon fiber, was activated for the release of a gaseous carbon source. In a second approach carbon fibers were coated with a catalyst-doped preceramic polymer and heated in argon atmosphere up to 900 °C. In both processes chemical vapor deposition (CVD) like conditions prevailed, and the growth of CNTs was observed on the surface of the carbon fibers.

This contribution reports for the first time the use of preceramic polymers to generate a hierarchical carbon nanofiber/CNT structure as a novel-type reinforcement phase. Results of both processes are compared with respect to the processing parameters and the amount of CNTs, and an outlook to future work will be given.

Keywords: *carbon nanotubes, carbon fibers, polymer derived ceramics, coating*

Elaboration of new generation of Carbide nanocomposites from preceramic polymer

Vanessa Proust^{1*}, Samuel Bernard¹ and Philippe Miele¹
vanessa.proust@univ-montp2.fr

¹ IEM (Institut Européen des Membranes), UMR 5635 (CNRS-ENSCM-UM2), Université Montpellier 2, Place E. Bataillon, F-34095 Montpellier, France

Today with the announcement of the depletion of fossil fuels, nuclear power which provides about 5.7% of the world's energy and 13% of the world's electricity can be one of the most promoted energy vectors for the future.

Within this framework, the future nuclear energy system, known as Generation IV, will provide manageable nuclear waste, effective fuel utilization, safety performance and secure systems and materials. These systems are to be deployable no later than 2030 in developed and developing countries, for generation of electricity and other energy products such as hydrogen for use as transportation fuel and fresh water for world regions facing future shortages. Six concepts have been selected for the 4th generation of nuclear systems (SFR, LFR, GFR, V/HTR, SCWR, MSR).

The fast breeder reactor use natural resources with less radioactive wastes but despite those advantages the working temperature between 800 °C and 1200°C of this reactor generation required a high melting point materials with high thermal conductivity under radiation to assure the minimal energy loss, such need can be a challenge on the materials developing fields.

Such applications impose to most often use specific materials with particular properties like composites or nanocomposites materials. Compositions, structures and shapes can be controlled by a non-conventional method called the polymer-derived ceramics route (PDCs) which is illustrated in figure 1.

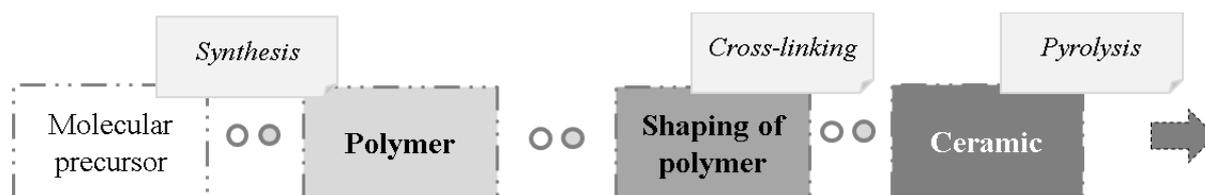


Figure 1: PDCs route, chemical process to elaborate non oxide ceramic

This method used preceramic polymers as ceramic precursor to be shaped, crosslinked then pyrolyzed to provide the targeted materials. Here, the targeted materials are silicon- and titanium-based carbide and nitride nanocomposites

In early 80's, nanocomposites were first used by Roy and Komarneni to describe heterogeneous materials obtained by sol-gel method. Then, in 1991, this concept was kept by Niihara to present nanostructured ceramic composite. Such materials are composed of two assembled phases: a first phase with at least one nanometric phase as a nanofiller and the other, named matrix which contains dispersed fillers. Herein, we propose to prepare bulk Si-Ti-C nanocomposites at relatively low

temperature in comparison to conventional processes, with a controlled *in-situ* segregation of Ti-based carbide nanophases during the elaboration of the amorphous SiC matrix.

In this presentation, we investigate SiC-based nanocomposite materials including different metal carbide-based phases such as TiC or MAX phase. The growing of the metal carbide nanophase in the SiC matrix is achieved by two ways through the polymer derived ceramics (PDCs) route (figure 2). We will present both strategies to prepare tailor-made carbide nanocomposites. The materials will be characterized at each step of their elaboration. Their application in nuclear reactors will be discussed.

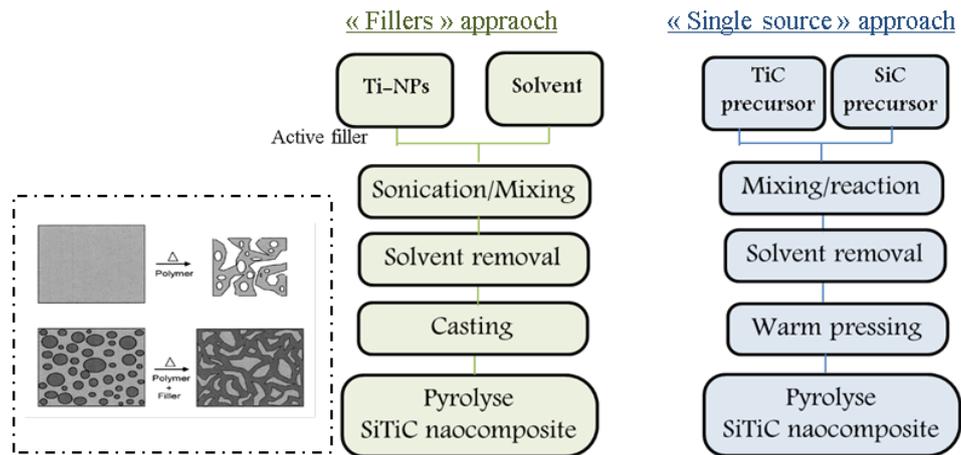


Figure 2: Elaboration of nanocomposite by two ways of polymer derived ceramics technic (PDCs)

SESSION 15

Processing and Properties of Silicate Ceramics

Porous and Dense Cordierite Ceramic from Raw Illite Clay

Maris Rundans¹, Ingunda Sperberga¹, Gaida Sedmale¹
marisr87@inbox.lv

¹Institute of Silicate Materials, Riga Technical University, Azenes Str. 14/24, Riga, Latvia, LV1048

Ternary system MgO-Al₂O₃-SiO₂ contains many technically valuable crystalline phases such as enstatite, forsterite, spinel and cordierite. For most of these phases coefficient of thermal expansion (CTE) is extremely low (as low as $1.5 \cdot 10^{-6} \text{ K}^{-1}$) which allows for them to be used in conjunction with other thermally demanding materials like quartz, for example. Also, other important properties like their high mechanical strength and good dielectric permeability is of value for potential use in practical applications. Cordierite ceramic materials, for example, are good candidates for both electronic circuitry substrates, when prepared as dense material and for use in filtration systems, when prepared as porous material.

Formation of cordierite from oxide powders takes place above 1350 °C. Rational preparation of such material requires modifications in synthesis rout, i.e., addition of flux forming agents or presence of volatile compounds. In this work the use of Latvian illite clay as partial raw material for preparation of both dense and porous cordierite ceramics was studied. No additional artificial flux and/or volatiles were used. Obtained dense ceramic samples were tested for their mechanical strength, and porous samples – for their pore morphology and porosity. It was determined that the use of illite clay of no less than 1/3 of total mass was enough to form both extremely dense and tough (compressive strength of about 400 MPa) and extremely porous (about 96% apparent porosity) materials by just adjusting thermal treatment regime. The X-Ray diffraction of the samples showed that formation of single-phase crystalline cordierite can also be achieved in relatively lower temperatures, e.g., as low as 1300 °C.

Keywords: *cordierite, spinel, porous ceramics, mechanical strength*

The Influence of Porosity on the Deformation Characteristics and Fracture of the Sintered Zirconia

Ekaterina Kalatur¹, Svetlana Buyakova¹, Sergey Kulkov¹
kalatures@mail.ru

¹Institute of Strength Physics and Materials Science of Siberian Branch Russian Academy of Sciences,
634055 Tomsk, Russia

Information about the behavior of porous ceramics under load is very important for its applications. In present work it has been studied a porous ceramics obtained from ultra-fine ZrO₂ powders. Samples were obtained by pressing and sintering of compacts, the porosity of ceramic samples was from 15 to 80 %. The structure of the ceramic materials was a cellular structure.

A distinctive feature of all the « σ - ϵ » diagrams obtained in the experiment was their nonlinearity at low deformations which was described by the parabolic law. Restructuring of deformation diagrams in double logarithmic coordinates allowed to determine the value of the exponent in deformation equation from experimental data. The increase of porosity in ceramics was accompanied with the increase of exponent, this fact may be associated with the change of deformation mechanism. The obtained values of the exponent for ceramic samples with a porosity higher than 25 % amounted to 3.5, which is probably due to a major contribution of the mechanical instability of ceramic cell elements in the ceramic carcass in the deformation process.

The studies found similarity in the mechanical behavior of high-porous cellular foam plastic and porous ceramic with cellular structure based on zirconium dioxide. This fact indicates that the observed nonlinear elasticity for low deformations on deformation diagrams is due to mechanical instability of the cellular elements in the ceramic carcass.

Keywords: porous ceramics, cellular structure, deformation, fracture.

The research was supported by the project of the RFBR № [14-08-31087\14](#), by President RF grants № MK-5681.2014.8, MK - 5883.2014.8

The Influence OF Clay Fineness Upon Sludge Recycling in a Ceramic Matrix

¹ Szoke A.M., ² Muntean M., ¹ Sandor M.
mariszoke@yahoo.com

¹ Faculty of Environmental Science Babes-Bolyai University, exten. Sf.Ggheorghe, Romania
² University "POLITEHNICA" of Bucharest, Faculty of Applied Chemistry and Materials
Science, P.O. Box 12-134, Bucharest, ROMANIA

To sustain a healthy life in harmony with nature, it is extremely important to develop various materials and processes that minimize any harmful influence on the environment. The feasibility of sludge recycling in the ceramic manufacture was evaluated through laboratory testing. Such residues have similar chemical and mineralogical composition with the raw mixture of the green ceramic body used in construction. Several ceramic masses with clay, sand and various proportion of sludge have been synthesized and then characterized by their physical-mechanical properties. The fineness of the clay, the main component of the green ceramic body, has been considered for every raw mixture. The proportion of the sludge waste addition depends of the clay fineness and the sintering capacity also, increases with the clay fineness. The ceramic properties, particularly, the open porosity and water adsorption and mechanical properties, in presence of small sludge proportion (smaller or equal 7%) shows small modification. The introduction of such waste into building ceramic matrix (bricks, tiles, and plates) has a very good perspective.

Keywords: *recycling, ecological ceramic, sludge in ceramic matrix, solid waste recycling*

Higher strengthened and lower brittle silicate ceramics

K. Boussois, N. Tessier-Doyen, P. Blanchart
nicolas.tessier-doyen@unilim.fr

Laboratoire GEMH-ENSCI - Centre Européen de la Céramique
12 rue Atlantis 87068 LIMOGES Cedex

A suitable microstructural organization of multiphase ceramic materials at the grain scale can improve significantly their macroscopic mechanical properties. In this work, silicate ceramics exhibiting a composite microstructure mainly composed of mullite phase have been elaborated from a small amount of long alumino-silicate fibres added to a kaolin powder. Thick substrates (about 700 μm in thickness) have been individually shaped by tape casting (aqueous suspensions) and then thermo-compressed in order to obtain multilayered materials with a promoted orientation of kaolinite sheets and fibres in the plane of tapes.

After sintering, the microstructure exhibits both initial added fibres (about 6 μm in diameter and more than 100 μm in length) and a significant amount of recrystallized acicular mullite crystals embedded in a silico-aluminate matrix phase. The amount, the size and the degree of microstructural organization mainly depend on experimental shaping and sintering parameters. Final materials present a highly anisotropic microstructure with different preferential orientations in particular along the fibres (perpendicularly to their surface) acting as templates to favour the growth of large mullite crystals. In these multilayered materials, the alumino-silicate matrix which is partly amorphous takes place at the beginning of the sintering (from 950 to 1400°C). On the cooling of the processing, almost all internal stresses are then accommodated even if anisotropic thermal expansion mismatches between the constituents are not negligible.

Elastic properties, level of strength and toughness are strongly correlated to the mullite degree of arrangement which has been characterized by SEM analysis. Despite the very low proportion of added fibres (less than 5vol.%), Young's modulus and bia-axial stress to rupture are improved of about 25 and 50% respectively. This higher fracture strength is mainly due to the interconnected network of mullite fibres and crystals at different scale levels of the microstructure. Moreover, toughness value is multiplied by 3 compared to the single substrate layer because of crack deflection and crack bridging mechanisms occurring at the fibre/matrix interface. Specific crack paths due to the anisotropic structure provide to these architectures a R-curve behaviour. These results emphasize that low cost silicate ceramics with significantly improved mechanical properties (both strength and toughness) can be obtained thanks to a very small addition of fibres and the use of processings devoted to organized the microstructure.

Keywords: *silicate ceramics, kaolin, tape casting, anisotropic properties, fibres, toughness*

Cement Kiln Dust/Rice Husk Ash as Low Temperature Route for Wollastonite Processing

Emad M. M. Ewais¹, Yasser M.Z. Ahmed¹, Ahmed A.M. El-Amir¹, Hamdy El-Didamony²
dr_ewais@hotmail.com

¹ Refractory and Ceramic Materials Division(RCMD), Central Metallurgical R&D Institute, P.O.87
Helwan, 11421 Cairo, Egypt

²Applied Inorganic Chemistry, Chemistry Dept., Faculty of Science, Zagazig University

The world cement production exceeds 3.6 billion tones. This quantity is accompanied by more than 7% cement kiln dust(CKD) as a byproduct. This waste is hazard materials and causes environmental problems. Egypt alone produces about more than 5 million tones CKD annually. On the other hand, there is huge quantities from rice husk ash(RHA) are produced annually as well. Therefore, finding of a practical and safe route for dispose of these wastes and their utilization in potential applications will avoid the society any environmental risks relevant to these wastes, save its energy and improve its economy. Wollastonite is very attractive candidate for wide range of industrial applications. The world wollastonite sales exceed 6 hundred thousand metric tons and its demand increases annually, however, the production from its available natural resource near to run out. The wollastonite demand is expected to be grown up to millions of tons annually if we succeed to find alternative resources. Fortunately, the proposed wastes in this study have the main constituents of wollastonite such as calcia and silica. The present study aims to determine the optimum conditions for the conversion of the cement kiln dust/rice husk ash into eco-friendly wollastonite. Different batch compositions from CKD and RHA were designed to prepare wollastonite. These batches were wet mixed, dried at 100°C for 24 hrs, grounded, sieved, uniaxially pressed and fired at different temperatures. Phase composition, microstructure, densification parameters, and mechanical properties of the obtained fired specimens were investigated. The results showed that α - & β -wollastonite polymorphs were synthesized successfully at lower temperatures (<1200°C) without addition of any mineralizers. The output of this work might be considered as one of the real solution for the environmental problem relevant to cement industry and rice husk ash.

Keywords: Wollastonite, cement kiln dust, RHA, sintering, FE-SEM, mechanical properties

Production of Refractory Chamotte Particle-Reinforced Geopolymer Composite

Tomáš Kovářik¹, Lucie Kullová¹, David Rieger¹
toko@ntc.zcu.cz

¹New Technologies - Research Centre, University of West Bohemia,
8 Univerzitní, Plzeň, 306 14, Czech Republic

Geopolymer resins are obtained by alkaline activation of aluminosilicate sources where raw calcined clays are one of the suitable potentialities. Besides the fact that chemical composition has an essential effect on final properties of the geopolymer binder, the type of filler strongly affected resulting properties of such granular composite. However, very few comparative studies have been done on detail description of composite systems: binder – granular filler, in relation to aggregate gradation design and rheology properties of the mixture.

The aim of this work is to develop and describe granular composite concerning workability of the mixture and kinetics of geopolymerization/polycondensation through flow behaviour. The rheological measurements indicated that initial viscosities of the mixtures and their evolution are different for various proportions of the filler. Moreover, it was demonstrated that increase in complex viscosity responds to the creation of chemical bonds and the formation of structural network. Finally, a correlation of the mechanism of geopolymer formation was carried out by differential scanning calorimetry (DSC).

Keywords: *geopolymer, composite, rheology, calorimetry*

Relationship Between Technological Properties and Stratification of "Lenti" (Hungary) Clay Deposit

¹László A. Gömze, ²Tibor Bokányi, ²György Benedek, ³Ralf Hermannsdörfer, ¹István Kocserha
femgomze@uni-miskolc.hu

¹Department of Ceramics and Silicate Engineering at University of Miskolc (Hungary)

²Creaton Hungary Ltd, Lentiszombathely (Hungary)

³Creaton AG GmbH (Germany)

Despite the modern building materials and technologies the conventional ceramic roof tiles are one of the most popular and most reliable roofing materials in our days also. It is obvious that the mineralogical composition of the used conventional brick clays as well as the stratification of the clay mines are very strong influences not only on properties of fired ceramic bricks and roof tiles but on efficiency and quality of the used technological equipment and processes. Now the modern technology lines of ceramic brick and roof tile plants are fully automatic and have very high production capacities. This large production accomplishment makes the ceramic roof tile plants very sensitive to the stratifications of clay mines and to preparedness of mined and used conventional ceramic and brick clays.

In the present work the authors have described and shown the influence of stratification of different mine layers on the following important physical and technological properties of the conventional brick clay from "Lenti" region of Hungary:

- Mineral structure and composition (XRD);
- Material structure and morphology (SEM and EDAX);
- Thermo-calorimetric properties (DTA, TG, DTG)
- Thermal dilatation and shrinkage of the conventional brick clay raw materials used in C for production of ceramic roof tiles,

Analytical methods applied in this research for tests of material structures were scanning electron microscopy, X-ray diffractions and energy dispersive spectrometry, laser dilatation tester and calory tester. Digital image analysis was applied to microscopy results to enhance the results of transformations.

Keywords: *brick clay, ceramics, dilatation, morphology, roof tiles, shrinkage, thermo-calorimetric properties.*

Glass Ceramic Foam based on Porcelain Raw Materials

Istvan. Kocserha, László. Fróna, László A. Gömze
istvan.kocserha@uni-miskolc.hu

Department of Ceramics and Silicate Engineering, University of Miskolc, Hungary

Glass ceramic foam was prepared from porcelain raw materials as kaolin, quartz sand and feldspar where Alunite mineral represented the foaming agents. The aim of this study was to investigate the developing mechanism of the foam's structure and the to characterize the foam product. According to the literature, the sulphur content of the alunite mineral departed up to 850°C, but sulphur in some ppm amount remained back in the decomposed structure of the mineral. The remained gas content departed only around 1300°C. The softening point of the mixture was set to the outgasing temperature so a foam structure with closed cells was produced. The XRPD analyses showed the presence of quartz, mullite and albite but the main phase was the amorphous content. The compressive strength of the foam was 1,2 MPa, the value of the density, the porosity and the coefficient of thermal conductivity were 0,6g/cm³, 62% and 0,1W/mK respectively. The water absorption of the foam was below 1%.

SESSION 16

Testing and Characterization of Materials and Methods, Equipment and Errors

Effect of bending velocity on release behavior of creased paperboard

Shigeru Nagasawa¹, Shinya Ozawa¹, and Yasushi Fukuzawa¹
snaga@mech.nagaokaut.ac.jp

¹Department of Mechanical Engineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan

Coated-recycled paperboard is considered to be a fundamental material for the packaging industry due to its advantages such as high strength-to-weight ratio, high surface smoothness, printability, sustainability, recyclability, and so on. To convert paperboard into a packaging container, the raw paperboard is first printed at a printing line. Then, it is subjected to cutting and creasing processes. The aim of these two processes is to convert the printed paperboard into a blank form before forming a glued box. Finally, the blank is folded and glued to obtain a packaging product. Since paperboard is a kind of composite material made of laminated thin papers and numerous fibers, its crease-based forming or shaping behaviors, especially the dynamic relaxation of folding resistance, are fairly complicated.

This work deals with the time-dependent creasing characteristics of coated paperboard. The correlation between the bending strength (resistance) and time-dependent problems on the actual processing phenomenon has not been sufficiently discussed in the past.

Quasi-static folding stiffness with respect to the indentation depth of the creaser was reported and also the crease deviation effect on the folding deformation of creased paperboard was discussed (Nagasawa, et al., 2001, 2003, 2008). However, the estimation of dynamic deformation behaviors of the creased line from the initial strength of the creased part, such as the first peak of bending moment and the first term gradient of bending moment, which are evaluated by one way motion, were not clarified. Recently, a new Crease Stress Tester (CST) was developed to seek the bending moment and also to record the side view image of a creased part during a repeated folding motion (Nagasawa et al., 2011). This testing device is able to control the bending rotation speed of the creased part of a worksheet and its sleeping time at a specified angle position (Katayama Steel Rule Die, 2013).

The knowledge of the dynamic bending moment (resistance) acting on a hinge which is folded onto a creased line, is important in order to adjust the mechanical conditions of the boxing stage performed by the automatic folder gluer machine. The correlation between the dynamic bending resistance and several primary problems such as the viscous-elastic residual strains on the actual processing phenomenon was not sufficiently discussed in the past. It is difficult to estimate various time-dependent responses from the quasi-static initial strength of the creased part, such as the maximum bending moment and the initial gradient of bending moment.

Therefore, the CST apparatus has been applied to seek the dynamic bending moment and its residual deformation. In order to reveal the relaxation characteristics of bending angle during the folding and returning back motion from a tracking angle of 90 degrees, a white-coated paperboard of 0.3 mm thickness was scored with a creasing rule and a grooved face counter plate under a specified

feed velocity, and then the bending and relaxation test was carried out up to the second round folding under a specified initial indentation depth (nominal shear strain).

Through this work, the followings are discussed: (1) The relaxation response of folded angle during returning back was characterized and approximated by an logarithmic function of elapsed time; (2) The relaxation of folded angle depends on the bending rotation velocity.

Keywords: *Paperboard, Bending, Folding, Velocity, Relaxation, Creep*

References

- [1] Nagasawa, S., Fukuzawa, Y., Yamaguchi, D., Nagae, S., Katayama, I. & Yoshizawa, A., Deformation characteristics on creasing of paperboard under shallow indentation, in: Proceedings of 10th International Conference on Fracture (Advances in Fracture Research, Elsevier Science), (2001), ICF10-0202OR-1-6, Hawaii, USA.
- [2] Nagasawa, S., Fukuzawa, Y., Yamaguchi, T., Tsukatani, S. & Katayama, I., Effect of crease depth and crease deviation on folding deformation characteristics of coated paperboard, *Journal of Materials Processing Technology*, 140, (2003), pp. 157-162.
- [3] Nagasawa, S., Endo, R., Fukuzawa, Y., Uchino, S. & Katayama, I., Creasing characteristic of aluminum foil coated paperboard, *Journal of Materials Processing Technology*, 201, (2008), pp. 401–407.
- [4] Nagasawa, S., Nasuruddin, M., Shiga, Y., Bending Moment Characteristics on Repeated Folding Motion of Coated Paperboard Scored by Round-Edge Knife, *Journal of Advanced Mechanical Design, Systems, and Manufacturing*, 5(4), (2011), pp.385-394.
- [5] Katayama Steel Rule Die Inc., The crease stress tester CST-J-1, online available from <diemex.com/sale/cst.html>, (accessed on May, 2013).

Physico-chemical and rheological characterization of water-based mud's in a polymers presence (PUC_UL and CMC)

B. Safi ¹, S. Zarouri ², R.Chabane-Chaouache ²
safi_b73@umbb.dz

¹ Research Unit: Materials, Processes and Environment (UR/MPE), Boumerdes University, Algeria

² Engineering Materials Department, Faculty of Engineering Sciences, Boumerdes University, Algeria

Under geological conditions of wells and during the drilling operation, some compositions of the Water-Base drilling Mud's (WBM), are sometimes not effective for the operation success of the drilling oil wells (The oil wells in the south Algeria). For this, this study aims to examine the influence of polymers of the type (CMC and PAC) on the physicochemical and rheological properties of water-based drilling muds. Mud's were elaborated polymers based (PUC_UL or CMC) according to mud formulations currently used in the wells drilling. Physico-chemical and rheological tests were carried out on these mud's. According to the obtained results, the rheological characteristics of studied mud's (yield point and plastic viscosity) were clearly improved in the polymers presence. However, it should be noted that the PUC_UL has given the better results compared to the CMC at a concentration of 8 g/L. Also, with this concentration and in the temperature presence (Hot-rolling), the CMC is a good controller agent of filtrate of mud compared to those containing the PUC.

Keywords: *Water-based-mud, polymer, CMC, PUC, rheology, yield point, viscosity, API filtrate.*

References

- [1] American Petroleum Institute. Principles of Drilling Fluid Control, 12th ed., I, University of Texas, Continuing Education Petroleum Extension service, Austin. (1969)
- [2] Baba Hamed S., Belhadri M.; Rheological properties of biopolymers drilling fluids, Journal of Petroleum Science and Engineering 67 (2009) 84-90.
- [3] Benyounes K., Benmounah A. Rheological and electrokinetic properties of carboxymethylcellulose-water dispersions in the presence of salts; International Journal of Physical Sciences, 2012, 7(11), pp. 1790 - 1798
- [4] Benyounes K., Mellak A., Benchabane A., The Effect of Carboxymethylcellulose and Xanthan on the Rheology of Bentonite Suspensions; Journal of Energy Sources Part A-recovery Utilization and Environmental Effects , vol. 32, no. 17, pp. 1634-1643, 2010

Physical and mechanical characterization of self compacting concrete with silica fume

Zerizer .A.¹, Kennouche .S.¹, Benmounah .A.¹ and Hami .B.¹
zerizer_ab@umbb.dz

¹ Research Unit: Materials, Processes and Environment (UR/MPE), University of Boumerdes

Self-compacting concrete (SCC) was elaborated using local materials and silica fume (SF) as admixture in 15% of cement quantity, two different Portland cements (PC) and two different superplasticizer that the chemical nature is polycarboxylate and plynaphthalene, the aggregates used are (AG 3/8 mm, AG 8/15 mm), coarse and fine sand (SC, SF) with fineness modulus 3.2 and 1 in the order. The dosage of the different superplasticizer used is chosen after experimental spreading tests of each self compacting concrete formulation. Results of fresh concrete tests executed, as L-box and segregation resistance are on concordance with values recommended by the French association of civil engineering. Also the mechanical characterization was conducted by compressive strength and splitting compression testing procedure, results values are in the range higher than 20 Mpa at the seven day by the compressive test for the all compositions, and the highest value was 40.93 MPa at the 28 day by compressive test of the fourth's formulation specimens, the values of splitting compressive tests of all formulation specimens at 7, 14 and 28 days, was situated between 2.01 and 4.40 MPa. In order to determine the superplasticizer saturation assay in of cement pasts used in self compacting concrete, the study was completed by a rheological study with a variable velocity gradient, so as to estimate the quantity of saturation assay of superplasticizer and the formulation, also the flow models of cement paste.

Key words: *Self-compacting concrete (SCC), silica fume, rheology, stress.*

- [1] Bouzoubaa N, Lachemi M (2001). Self-compacting concrete incorporating high volumes of class F fly ash: Preliminary results. J. Cem. Concr. 31:413–20
- [2] Malhotra VM, Mehta PK (2002). High-performance, high-volume fly ash concrete. Suppl. Cem. Mater. Sustain. Dev. Inc. Canada, 24(7):30-34.

Possible method for determination freeze-thaw resistance of porous material

Sergey Nikolskiy¹, Olga Pertseva²
olya_perceva@mail.ru

¹Department of Construction designs and materials, St. Petersburg Polytechnical University, 195251 St.Petersburg, Russia

² Department of Unique buildings and constructions, St. Petersburg Polytechnical University, 195251 St.Petersburg, Russia

Task of project is substantiation of new method for determining freeze-thaw resistance of porous water-saturated materials, for example, concrete. Offered method makes good defects of latest methods, is characterized small labour input and high operability. Also it has wide field for application, because this method is good for many types of porous materials. It is based on dimension some permanent sets ε , such as permanent set after some freeze-thaw cycles ε_t and permanent set after mechanical pressure of specimen in perpendicular to previous pressure direction ε_m . Freeze-thaw testing was carried out in a dilatometer.

It has been established that permanent set ε depends on number of cycles c as per exponential function $\varepsilon = A c^\lambda$ (1), where A is permanent set after first cycle, λ is material constant (is determined by test). According to experiment, such relation has good approximation. If take into account that freeze-thaw resistance of specimen is equal maximal number of freeze-thaw cycles and $\varepsilon_t = \varepsilon$, make similar speculations for mechanical pressure, freeze-thaw resistance of specimen will be calculated as per (1) after some mathematical manipulations of that.

To prove method correctness it was realized on 10 concrete specimens. Age of specimens consolidation is 88 days. Specimens of concrete mortar were prepared using a mix of portland cement 400 (12,3%), sand of dimensions 0.6-5 mm (24,7%), granite macadam of dimensions 5-20 mm (55,4%) and water (7,4%). Freeze-thaw resistance such mortar was determined earlier by method, approved national standard specification, it was equal 105 cycles. According to dimensions by new offered method freeze-thaw resistance such mortar is equal 107 cycles and its confidence interval is equal 5,4 (probability $P = 0,95$). Therefore, spread of results could be casual and offered method is correct.

Keywords: concrete, freeze-thaw resistance, permanent set, durability, monitoring of strength, freeze-thaw cycling

Rheological Model for Polymeric Fluids Flows in a Channel with a Square Cross-section with Slipping Phenomena

Pyshnograï Ivan
pyshnograï@mail.ru

Department of Mathematics, Altai State Technical University, Barnaul 656031, Russia

A large number of liquid systems, among which polymeric and bio-polymeric materials, reveal the anomaly of slipping often near the solid surface. The consequence of this phenomenon is a violation of the hypothesis of stick in the wall and the need to determine the appropriate boundary conditions.

Such anomalous behavior of materials in a plastic state (slurry, grease, fluids and polymer melts) at solid surfaces requires a comprehensive study of both rheological properties and calculating the flow parameters and characteristics of the processing equipment. In the first place, there is a complex problem of determining the rheological properties of the material in accordance with the results of viscometric studies. The next stage is associated with specific problems on the motion of fluids, which have this feature on solid surfaces, and the direct use of sliding velocities as boundary conditions.

This work is to specify explicitly the slip velocity at the wall, which is generally a function of stress at the wall, the geometric dimensions and temperature. This dependence of slip velocity at the wall of these factors founded from viscometric measurements.

Next considering the case of flow Poiseuille flow with allowance for slippage of the polymer material at the boundary, the system of equations of the modified rheological model Vinogradov and Pokrovskii describes non-parabolic velocity profile in the gap between parallel plates, which experimental data confirmed.

The dependences obtained will used for study of more complex flows. This illustrated by calculating the three-dimensional velocity profile of a nonlinear viscoelastic fluid through a duct with a square cross-section.

During execution of the following results: obtained flow characteristics of plane channel in the presence of slip on the border, formulated nonlinear boundary conditions of the third kind of slip velocity, obtain three-dimensional velocity profile and the stress tensor components of nonlinear viscoelastic fluid in a channel with a square cross-section as a function of the parameters of the rheological model and the pressure gradient. Shows the possibility of using a modified rheological model Vinogradov Pokrovskii for describing three-dimensional flow solutions and melts of linear polymers based on slip at the wall.

This work was supported by the Russian Foundation for Basic Research № 12-01-00033.

Keywords: *rheology, slipping phenomenon, polymer melts, mesoscopic approach*

New method of determination of spot welding-adhesive joint fatigue life using full field strain evolution

Tomasz Sadowski¹, Marcin Kneć², Przemysław Golewski¹
 m.knec@pollub.pl

¹Lublin University of Technology, Department of Solid Mechanics, Nadbystrzycka 40 Str., 20-618 Lublin, Poland

²Lublin University of Technology, Civil Engineering Laboratory, Nadbystrzycka 40 Str., 20-618 Lublin, Poland

Spot welding-adhesive hybrid joints are widely used in aerospace industry, for example to stiffening of the aircraft fuselage plate elements. This joint type is obtained by spot welding and fills the space between an angle and aluminum sheets by an adhesive, Fig. 1.

During a flight an airplane is subjected to high frequency cyclic loading. Therefore to estimate the fatigue response of structural joints it is necessary to perform the Wöhler – S-N curve tests (standard approach) to find a fatigue life and strength. This work requires many specimens and long experimental time. This paper proposes a new approach to reduce machine time and number of specimens for characterization of the joint behavior.

The idea of the method relies on estimation of damage accumulation during fatigue loading. Tests were performed for increased of the semi-amplitude level of the load spectrum (Fig 2). Experiments were continued up to the final failure of the joint (Fig. 1) to get the fatigue strength. The fatigue tests were performed for a real load spectrum of aircrafts recorded during real airplane flight in PZL Mielec factory (Poland).

Figure 1 shows specimen dimensions and shape, whereas Fig. 2 – the load spectrum with increase of the semi-amplitude load level.

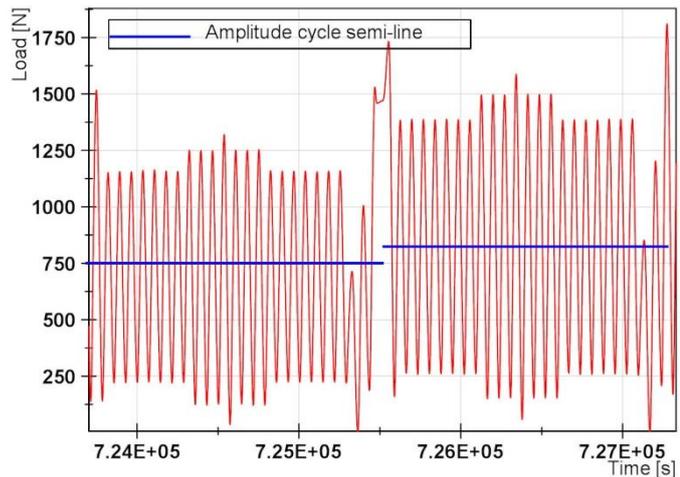
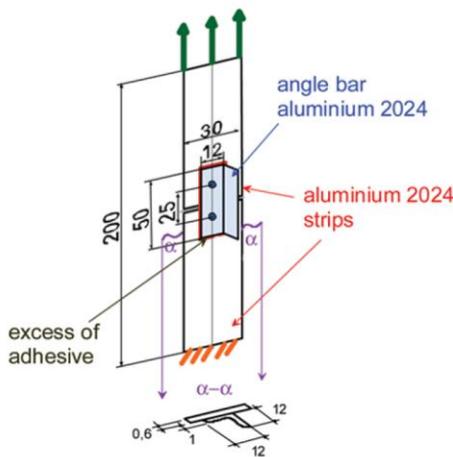


Fig. 1 Specimen shape and dimensions Fig. 2 Increases of the semi-amplitude level of the load spectrum

Evolution of the full field strain was recorded by application of the Digital Image Correlation system (ARAMIS). Two synchronized sensors of the DIC system were used in both sides of specimens to monitor strains fields during the whole deformation process up to the final failure.

Results presented in this article prove that using full field strain evolution measurement allows for assessment of the fatigue life and strength with application of significantly less number of specimens.

Experimental results were verified by numerical FEM analysis with application of the fatigue damage model. The numerical results confirm testing observations and allow for specification of the most damaged regions of the joints during fatigue process.

Keywords: *HSW, DIC, rapid determination, fatigue life, Aramis, hybrid joint.*

Effects of the feedstock preparation on the ceramic injection molding process and the quality of end product

Adam Egesz^{1,2}, Viktória Veréb¹
adam.egesz@ge.com

¹Department of Ceramics and Silicate Engineering, University of Miskolc, Miskolc, Hungary

²GE Hungary Ltd., Budapest, Hungary

In the illuminant industry, the ceramic arc tube parts are made of high purity alumina powder, and for producing these parts for high intensity discharge lamps, the applied method is the ceramic injection molding. It is very important to set up an appropriate injection molding process to get a high quality product. But, first of all, we need to know the properties of the injection molding raw material, and optimize them in order to get the proper raw material composition for the highest quality end product.

For producing ceramic arc tube parts (plugs), there are used two different major components for producing injection molding raw material (feedstock): high purity alumina powder as the main component, and an organic paraffin wax as a binder material. To know and set up the mixing conditions of these materials is a momentous factor to get a ceramic product without cracks, spots or any other failures.

In this study, a design of experiment was prepared, in which as factors, the main settings of the mixing process were varied, (mixing time, temperature, additive materials, etc.) and the prepared raw materials were tested by injection molding, to check the quality of end product. the Applied analytical methods were capillary viscosity and rheological analysis, scanning electron microscopy, density measurement and laser granulometry. In addition, the end products were tested by dimensional and visual inspection.

Keywords: *alumina powder, paraffin wax, ceramic injection molding, laser granulometry, scanning electron microscopy, rheology analysis*

Influence of cutting conditions on milling of thin-walled parts

Alexander Isaev¹, Vladimir Grechishnikov¹, Mihail Kozochkin¹,
Marina Volosova¹, Yuriy Petuhov¹
avisz@yandex.ru

¹ Moscow State University of Technology "STANKIN", 127994 Vadkovskiy pereulok, 3a,
Moscow, Russia

The development of milling technological process for machining of thin-walled workpieces is a serious problem. The cutting conditions and the type of machining dramatically influence roughness and form deviations of end product. Experimental milling cuts of parts with different thickness of the walls were performed. Vibroacoustic signal recorded during the machining process was used to make recommendations of how improvements of the quality of thin-walled parts can be achieved.

Keywords: *Diagnostics of Machining Process, Milling, Thin-Walled Parts, Vibroacoustic Test.*

Special cutting head for lathe cut-off and grooving parts of various shape

Alexander Isaev¹, Vladimir Grechishnikov¹, Grigoriev Sergey¹, Petr Pivkin¹, Yuriy Petuhov¹
avisz@yandex.ru

¹ Moscow State University of Technology "STANKIN", 127994 Vadkovskiy pereulok, 3a, Moscow, Russia

The paper considers an approach to designing and description of unique construction of cutting heads used for lathes to machine grooves with a wide range of diameters and inclination angles of conical groove's generatrix.

Keywords: *Lathe Tool, Lathe Grooving Tool, Lathe Part-Off Tool, Cutting Tool Design.*

The Meaning of Zeta Potential for Solid Surface Characterization

Christine Onitsch¹, Thomas Luxbacher¹
christine.onitsch@anton-paar.com

¹Anton Paar GmbH, 8054 Graz, Austria

The zeta potential describes the surface charge of a solid when it gets in contact with a liquid. It is an important parameter for every solid surface which gets in contact with water during its application, e.g. membranes used for water treatment, biomaterials in contact with blood, semiconductor wafers which get cleaned with aqueous solutions. The zeta potential gives information on the surface chemistry, i.e. the presence of functional groups on the outermost surface layer of a material. It gives indication for acidic or basic behaviour of a surface in contact with an aqueous solution and provides information on the interaction of dissolved substances in solution with the sample surface in terms of liquid-on-solid surface adsorption processes. Knowledge of zeta potential of a material helps to optimize specific surface modification processes for a material to perform at its best in its application.

For solid surfaces, the zeta potential is determined from streaming potential or streaming current measurements. When a liquid is forced to flow through a small channel formed between two plates of the solid sample, surface-charge compensating ions are sheared off their equilibrium position and an electrokinetic effect called streaming potential forms at the solid-liquid interface. The streaming potential signal can be detected by two Ag/AgCl electrodes placed in close vicinity to the streaming channel. The zeta potential is proportional to the slope dU/dp of the linear relationship between streaming potential and applied pressure.

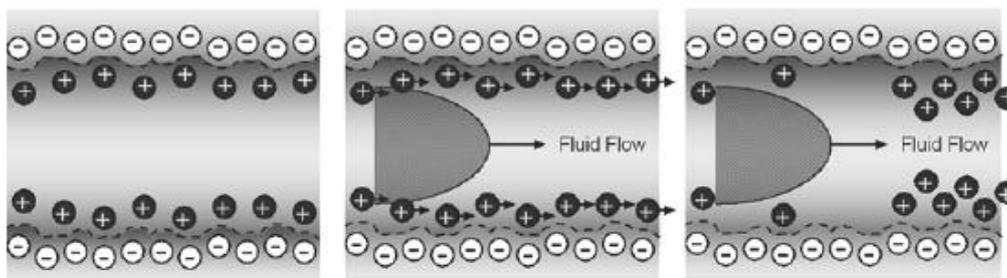


Fig. 1: Schematics of streaming potential

For the present work, SurPASS electrokinetic analyzer was used to assess the zeta potential of various substrates. Exemplary results on the pH dependence of zeta potential as well as adsorption kinetics will be presented, thereby highlighting the importance of zeta potential analysis for solid surface characterization.

Keywords: *zeta potential, surface charge, surface modification, surface functionality, electrokinetics, streaming potential technique, liquid-on-solid adsorption processes*

Relative Importance of Pore Parameters in Compressive Strength of Ceramics

Matti Järveläinen¹, Arto Ojuva², Erkki Levänen¹,
matti.jarvelainen@tut.fi

¹Department of Materials Science, Tampere University of Technology P. O. Box 589, FIN-33101
Tampere, Finland

²Department of Materials and Environmental Chemistry, Stockholm University, Stockholm 10691,
Sweden

The mechanical strength of a ceramic component is dictated by its microstructure, and based on Griffith's theory; the fracture strength is limited by the component's critical flaw size. In addition to the flaws, porosity also controls the compressive strength because decrease in porosity means that there is more bulk material under the load. Even though the total porosity in many cases is the major parameter affecting compressive strength, the shape and size of the pores also have to be taken into account.

The relative importance of these variables is investigated in this research. The study is carried out by preparing ceramic samples with identical porosity but with different pore characteristics, such as pore shape. The pores are characterized and the compressive strength is measured. The different variables that describe the pores are compared against the compressive strength in order to find the relevant factors and their relative influence to the total compressive strength of the structure.

Keywords: *Pore characterization, mechanical strength, pore parameters, compressive strength*

A Meshless Element-Free Galerkin Algorithm for Nonlinear Electromagnetic Field Computation

Leila Chelghoum¹, Kamel Zidani²
Chelghoum_leila1970@yahoo.fr

¹Department of Electrical Engineering, University Hadj Lakhdar, Batna, Algeria

²Department of Mechanical Engineering, University Hadj Lakhdar, Batna, Algeria

The magnetic hysteresis phenomenon of ferromagnetic cores influencing not only the distribution of the magnetic field, but also the waveform of the voltage and current of the linked electrical circuit. Hence, the prediction of the electromagnetic behavior is an important tool for the design of electrical devices. Modeling of ferromagnetic materials hysteretic behavior is essential for an effective and reliable integration in electrical engineering computations. It allows more realistic simulations and therefore an appropriate design taking into account the losses caused by the nonlinear behavior of ferromagnetic materials. In recent years, the scientific studies number dedicated to the modeling of hysteresis and losses computations is continually increasing. This paper outlines a numerical procedure based on the magnetic field computation taking the hysteresis into account. The scalar Preisach model is integrated into a meshless element-free Galerkin (EFG) method analysis. The hysteretic nonlinearity is handled by the fixed point iterative technique. Detailed of mathematical derivations and numerical implementation focusing on the convergence criteria are discussed. The developed algorithm was applied to study an electromagnetic device containing a ferromagnetic core. Numerical simulations highlight, among other, the power of the EFG method in terms of time computation and accuracy. Obtained results were compared to those provided by finite element (FE) method.

Keywords: *Hysteresis, nonlinearity, meshless method, element-free Galerkin method, Preisach model, fixed point technique*

Crack Formation in Cement-Based Composites

Andina Sprince¹, Leonids Pakrastinsh² and Nikolai Vatin³
andina.sprince@rtu.lv

^{1,2} Department of Structural Engineering, Riga Technical University, Kalku 1, Riga, LV-1046, Latvia

³ Institute of Civil Engineering, Saint-Petersburg State Polytechnical University, Politekhnikeskaya 29, 195251 St Petersburg, Russia

The cracking properties in cement-based composites widely influences mechanical behavior of construction structures. The challenge of present investigation is to evaluate the crack propagation near the crack tip. During experiments the tension strength and crack mouth opening displacement of several types of concrete compositions was determined. For each composition the Compact Tension (CT) specimens were prepared with dimensions 150x150x12mm. Specimens were subjected to a tensile load. Deformations and crack mouth opening displacement were measured with extensometers and analyzed using a digital image analysis technique to gain detailed insight in the cracking process during the initiation, formation and the opening phases. The formation and propagation of the tensile cracks was traced on the surface of the specimens using a high resolution digital camera with 60 mm focal length. Images were captured during testing with a time interval of one second. The obtained experimental curve shows the stages of crack development.

Keywords: *Crack propagation, Image analysis, Tensile strength, concrete*

Novel applications of microwaves in the metallurgical processing of a nickeliferous laterite ore and an aluminum industry waste (red mud)

Michail Samouhos¹, Maria Taxiarchou¹, Evangelos P. Kouvelos²
msamouhos@metal.ntua.gr

¹Laboratory of Metallurgy, School of Mining and Metallurgical Engineering, National Technical University of Athens, Zografou Campus, Athens, Greece

²Demokritos National Center of scientific research, Agia Paraskevi, Attiki, 153 10, Athens, Greece

Microwave radiation is a relatively new source of energy in the pyrometallurgical processing. The most significant advantages of microwaves are; (a) the direct heating in the interior of the materials, (b) the development of high temperatures in combination with high heating rates, and (c) the low thermal losses. In the current study, the application of microwaves in the carbothermic reduction of a nickeliferous hematitic laterite ore and the reductive roasting of a red mud were investigated. The effective microwave heating (at temperatures above 900 °C) of the above materials is attainable due to the relatively high values of their imaginary permittivity (ϵ''). The average power (P_L) absorbed by a material per unit volume is estimated by:

$$P_L = \frac{1}{2} \omega \epsilon_0 \epsilon_r''(T) |E_{\text{int}}|^2 \quad (\text{watts/cubic metre})$$

Where: ω , is the angular frequency ($2\pi f$, in radians- s^{-1}), E_{int} , is the internal electric field in the sample (Vm^{-1}) and ϵ_0 , is the permittivity of free space.

In both two cases, the reduction of the included hematite (Fe^{+3} to Fe^0) was attempted, and the reduction degree was calculated as a function of; (a) the heating time, (b) the amount of the supplied microwave power, (c) the amount of carbon content and (d) the sample's mass. It was found that about 70% reduction degree is achieved after 8 min of heating using 800 W of microwave power in the case of laterite, while about 59% reduction degree was achieved after 12 min of heating at 1000 W in the case of red mud. The mechanism of the Fe^{+3} to Fe^0 conversion was investigated using Mössbauer spectroscopy showing the formation of magnetite, fayalite and nano-structured metallic iron. In addition, the reduced samples were examined using X ray diffractometry and scanning electron microscopy. Finally, it should be noted that is the first time in bibliography that the gaseous products of a microwave pyrometallurgical process are analyzed using a mass spectroscopic technique

Chalcohalide Glass-ceramics Characterized by Positron Annihilation Technique

Halyna Klym¹, Adam Ingram² and Oleh Shpotyuk^{3,4}
klymha@yahoo.com

¹Lviv Polytechnic National University, 12 Bandery str., Lviv, 79031, Ukraine

²Opole University of Technology, 75 Ozimska str., Opole, 45370, Poland

³Lviv Institute of Materials of SRC "Carat", 202 Stryjska str., Lviv, 79031, Ukraine

⁴Institute of Physics of Jan Dlugosz University, 13/15, al. Armii Krajowej, Czestochowa, 42201, Poland

Chalcohalide glasses (ChHG) and glass-ceramics receive considerable interest for their particular properties leading to numerous applications in different domains such as optical, communications, infrared sensing, etc. One of the best techniques capable to probe free volumes in solids is the positron annihilation lifetime (PAL) technique. The PAL technique in the measuring mode of Doppler broadening of annihilation line (DBAL) allows additional identification of positron trapping sites possible in the tested objects. In this work, we shall analyse possibilities of PAL and DBAL technique to study free-volume entities in $(80\text{GeS}_2-20\text{Ga}_2\text{S}_3)_{100-x}(\text{CsCl})_x$ glass-ceramics with $x = 0;5;10;15$.

The PAL spectra were recorded with conventional fast-fast coincidence system (ORTEC) at the temperature $T = 22\text{ }^\circ\text{C}$ and relative humidity $\text{RH} = 35\%$, provided by special climatic installation. The measured PAL spectra of ChHG were processed with standard LT 9.0 computer program, the obtained curve being fitted by two components with τ_1 , and τ_2 lifetimes and I_1 , and I_2 intensities. The positron trapping modes in the studied ChG, e.g. average positron lifetimes τ_{av} , positron lifetime in defect-free bulk τ_b , positron trapping rate in defects κ_d and trapping rate in defects κ_d and fraction of trapped positrons η were calculated using a formalism of known two-state positron trapping model. The experimental system for DBAL measurements was arranged like in PAL geometry using high-purity Ge detector with an energy resolution of 1.54 keV at 511 keV. The shape of the 511 keV annihilation line was treated in terms of so-called S and W parameters.

It is shown that defect-related lifetime τ_2 demonstrates slight increase from 0.429 ns in GGS-CsCl0 samples to 0.466 ns in GGS-CsCl5 sample, while the I_2 intensity roughly drops from 0.38 to 0.34 ns. These strong changes reduce the trapping rate of defects κ_d mainly due to decrease in I_2 intensity. With further CsCl content in the studied ChHG, the κ_d parameter drops continuously from 0.72 in (GGS-CsCl5) sample to 0.59 ns^{-1} in (GGS-CsCl10) sample. It is obvious that atomic densification caused by CsCl additives to base ChHG depresses positron annihilation trapping rate leading to significant inhibition in the positron trapping coefficient κ_d value.

It is shown that PAL and DBAR technique can be used for study of free-volume changes in Ge-Ga-S glass matrix caused by CsCl additives. The results testify in a favor of rather unchanged nature of corresponding free-volume voids responsible for positron trapping in the studied glasses, when mainly concentration of these traps is a subject to most significant changes with composition.

Keywords: positron trapping, free-volume entities, chalcohalide, glass

An efficient method for solving the coupled equations of MAS (Müller, Achenbach and Seelecke) model

Kamel Zidani¹, Mourad Abdelhamid¹ and Leila Chelghoum
kzidani05@gmail.com

¹Department of Mechanical Engineering, Faculty of technology, Batna University, Batna
Algeria
Laboratory of Innovations in Eco-Design of Structures and Seismic Mechanical

Shape Memory Alloys (SMA) are metallic alloys that exhibit unusual specific properties such as memory effects and pseudoelasticity. In high-tech industries, the ability of shape memory alloys to cover large deformations and the high mechanical energy density are the most used properties. The exceptional material behavior of SMA is based on martensitic phase transitions, which can be initiated and propagated by thermomechanical processes. Martensitic phase transitions take place without diffusion processes. These phase transitions are the result of cooperative movements of atomic layers until the crystal structure of the product phase is reached. When loaded, the structure of a SMA sample oscillates between two phases: a highly symmetric austenite phase and a less ordered twinned structure called martensite. Under uniaxial loading conditions, three different phases can be observed in a shape memory alloy: the austenitic phase "A" and two martensitic twin variants " M_{\pm} ". SMA exhibit a highly nonlinear and hysteretic constitutive behavior with strong thermo-mechanical coupling. It is important to have efficient mathematical models reporting on the different SMA observed behaviors. In the literature, several studies have been devoted to the mathematical modeling of thermomechanical behavior of SMA. Among the models capable of incorporating the according thermomechanical coupling between the mechanical and thermal constitutive equations is the one named after Müller, Achenbach and Seelecke (MAS model).

In this work, after a brief overview of the martensitic transformation, we introduce the MAS mathematical model and we develop by using a mathematical formalism integrating Laplace transforms, a new efficient methodology for resolution of the coupled equations. This new solving approach allows a large gain in computer time and a better control of the salient behaviors observed in SMA such pseudoelasticity. Also, this new solution methodology avoids the heavy computing formalism related to the implementation of the model in computer codes. Subsequently we present and discuss results of various numerical simulations obtained by using a Maple developed program.

Keywords: *shape Memory Alloys (SMA) - martensitic phase transitions - austenitic phase – martensitic phase - nonlinear and hysteretic constitutive behavior - thermo-mechanical coupling - numerical simulations*

Microstructure Prognosis Within The Fractal Perspectives

V.V. Mitic^{1,2}, Lj. Kocic¹, V. Paunovic¹, F. Bastić¹, D. Sirmić¹, M. Cvetanović¹,
vmitic.d2480@gmail.com

¹University of Nis, Faculty of Electronic Engineering, Nis, Serbia

²Institute of Technical Sciences of SASA, Belgrade, Serbia

Sintering process is a complex of different synergetic effects during the ceramics materials consolidation. The structure of doped BaTiO₃-ceramics materials can be controlled by using different sintering parameters. An influence of additives concentration on microstructure and dielectric properties of doped BaTiO₃-ceramics is developed, based on fractal geometry. The microstructural level properties control is very important as a stage in advanced materials prognosis. Coble's two-sphere model is used as initial one for developing a new two-ellipsoid model. The reason is that the ellipsoidal geometry can better approximate sintering particles than spherical one. In this paper, the relations connecting geometric parameters of the ellipsoidal model, with consolidation parameters-sintering time and temperature, are established. In this research, different concentration of Ho₂O₃ additive are used. The ratio of dopant concentration ranges from 0.05% to 1%. The sintering temperature of 1350°C is chosen. The grains contact models based on spherical, ellipsoidal and polyhedral geometries are reviewed. Intergranular impedance analysis of grains clusters and fractal method was also introduced. Fractal method paves a new approach for analysis the structure of ceramics, describing and prognosis and modeling the grains shape and relations between BaTiO₃-ceramics structure and dielectric properties. These fractal effects and fractal materials nature have been used for better understanding interrelation between structural and electrical parameters.

Keywords: BaTiO₃-ceramics, doped ceramics, fractal structure, Coble's model, microstructure

The effect of successive repairs on the weldment quality of API 5L X-70 pipeline steel H.S.L.A.

¹Bouzid Maamache, ²Abdelhalim Brahimi, ³Mabrouk Bouabdellah,
¹Brahim Mehdi, ¹Youcef Yahmi
b.maamache@csc.dz

¹Welding and Non destructive Testing Research Center (CSC),
Metallurgy and Mechanical Division, BP 64, Route de delly brahim Algiers DZ

²University SAAD DAHLAB Blida, Méchanical Engineering, BP 270 BLIDA (09000) ALGERIE Route
De Soumaa Blida DZ

³The National Polytechnic School (ENP), Department of Metallurgy, Avenue Hacén Badi Elharrach/
Algiers DZ

The aim of this work is to study the influence of successive repairs on the microstructure and mechanical properties of HAZ in a welded HSLA steel API 5L X70, used in crude oil or natural gas transport. Due to the regeneration of the HAZ microstructure after each repair, the results show that the succession of repairs in the same area has no influence on the microstructure morphology for all the welded joints samples. However, based on the X ray diffraction analysis (XRD) using the MAUD software to characterize the crystallite sizes, the micro-strain and the dislocation density, the results show an outstanding evolution in microstructural parameters in the HAZ, i.e. an increase in the coherent domain sizes of diffraction and a decrease in the micro-strain and dislocation density according to the repairs number. The obtained values of the tensile strength of the various welded pipes are acceptable by the standards which imply the qualification of the welding process for all the repairs. Therefore, the previous investigations lead to the conservation of the same mechanical properties, i.e. the possibility of making more repairs that the standards specify.

Keywords: *Welding, Heat affected zone, XRD, thermal cycles, HSLA*

Mechanical property and characterization of metallic bond coat used in hardfacing of petroleum drill bits

¹Youcef Yahmi,, ¹Reda Badi, ¹Bouزيد Maamache, ²Djamel Miroud
y.yahmi@csc.dz

¹Welding and NDT Research Center, Metallurgy and Mechanical Division
²University of Science and Technology Houari Boumediene,
Faculty of Mechanical Engineering and Engineering Processes

Tungsten carbides are widely used as weld hardfacing deposits in petroleum drill bits. To assure proper bonding of the hardfacing to the substrate, several choices of bond coating layers are offered. In this study, tow different commercial powders A and B and mixtures of both them were thermal sprayed onto a carbon steel XC18 substrate used in petroleum drill bits. The micro hardness respectively, of the hardfacing surface and bond coating layers was measured. The microstructure was observed by optical microscopy and field emission scanning electron microscope equipped with energy-dispersive X-ray spectrometry. It has been observed that the mixture of 75% of A and 25% of B produces an uniform coating metallurgically bonded to the substrate with a little heat affected zone and a little amount of porosity.

Keywords: *Thermal spray coating; drill bit; Bond coat layer; weld hardfacing; Adhesion*

is-icm1

**The 1st International Symposium on Innovative
Construction Materials**

Distribution of air ventilation systems auditoriums

Ayrat Yunusov
yunusovairat@mail.ru

Civil Engineering Institute, Saint Petersburg State Polytechnical University, 195251 Saint Petersburg, Russia

Organization of air distribution in large auditoriums is a complex task, which is only possible in the course of joint activity of designers, designers, acousticians, designers and other professionals. Equally important is the choice of alternative vozduhorazdayuschih devices (ASP) meeting the requirements of comfort, design and a design room. The article describes an approach to this problem based on foreign experience.

Calculations performed two types of vortex and perforated the device ladder air diffuser.

Data analysis allows the calculation of state :

1. Application eddy DLADs , due to the higher efficiency of mixing the air , compared with perforated DLADs makes feeding into the working zone , without deterioration of comfort, colder air .

2 . eddy DLADs compared with perforated DLADs have lower flow resistance . When balancing the DLADs installed directly to long ducts, low hydraulic resistance is a negative factor . It makes increase the diameter and reduce the length of the duct . Furthermore, eddy DLADs unlike perforated DLADs not completed flow regulators .

3 . eddy DLADs form jets with higher compared with perforated DLADs , the degree of turbulence in the flow. In accordance with DIN 1946 part 2 , increasing the flow turbulence intensity c 5 to 20 % is necessary to reduce the mobility of the air by 30 % . That is, with the same mobility in a stream of air perforated DLADs provide better compared with eddy DLADs comfort .

Keywords: *the device ladder air diffuser, acoustics of the hall, dissipation and air flow required, absorption coefficient of the noise in the room*

Investigatory Experiments in Use of Organic Fibre (Newsprint material) Reinforcement in Portland Cement Concrete Mix Design

Kamran Haider Naqvi¹, Mansoor Imam², Hassan Ahmed³
imam386@gmail.com

¹Pakistan Sustainable Transport Project, International Union for Conservation of Nature & Natural Resources, 1 Bath Island Road, Karachi-75530, Pakistan

²Waste Management, Independent Environmental Consultant, Karachi-75530, Pakistan

³Department of Civil Engineering, Sir Syed University of Engineering & Technology, Karachi-75300, Pakistan

An exploratory research work at the Department of Civil Engineering was carried out by a group of final year undergraduate students who investigated into the possibility of utilising newsprint waste into concrete mix as reinforcement harnessing the tensile strength of its organic fibre made of lingo-cellulosic material. The concept was to shape the paper material into bar forms or sticks having certain stiffness to be cast in the concrete mass. The vertical and horizontal placement of reinforcement as mesh conventionally placed in slab of 2 ft square by 1 to 2 inch thick having the ordinary concrete mix design was experimented for load test after normal curing time. The results indicate that the maximum and minimum loads under compression testing by universal testing machine the peak stresses recorded are in the range of 6.60 to 11.53 psi which depends upon the configuration of paper reinforcement, the combination and manner in which the reinforcement bars have been prepared from the newsprint paper.

Keywords: *Innovations, Concrete, Paper reinforcement, Recycling, Reutilisation, Paper Waste, Reinforcement Concrete, Fibre Reinforce Concrete*

Fracture Behaviour Of Glass Columns

András Jakab¹– Kinga Nehme²– Salem Georges Nehme³
jakab.andras@epito.bme.hu

¹Phd Student, Department of Construction Materials and Engineering Geology, Budapest University of Technology and Economics, Budapest, Hungary

²Associate Professor, Department of Civil Engineering, University of Debrecen, Debrecen, Hungary

³ Associate Professor, Head of the Laboratory, Department of Construction Materials and Engineering Geology, Budapest University of Technology and Economics, Budapest, Hungary

Nowadays supporting structures can be transparent due to the development of glass strengthening procedures. The building glass as a versatile building material enables the efforts of the architects due to its transparency. This paper focuses on glass columns in the topic of load-bearing glasses and also on the design and load bearing capacity of fins and stability issues. Laboratory experiments were carried out at the BME, Department of Building Materials and Engineering Geology on the fracture behaviour of centrally compressed glass columns. More than 60 specimens were loaded until fracture. The load and deformations were measured. Based on the experimental results the critical force was determined and with force-deflection diagrams were illustrated the fracture and stability processes. The results were analysed with the calculation procedures in the focus of the international literature. Authors are going to compare the results of the laboratory experiments and theoretical calculations.

Keywords: *glass column, buckling, load bearing glass, stability, transparency*

Innovative materials for passive fire protection of tunnels

Konstantinos-Miltiadis Sakkas¹, Dimitrios Panias², Pavlos Nomikos¹, and Alexandros Sofianos¹
sakkas@metal.ntua.gr

¹Department of Tunnelling, National Technical University of Athens, Athens 15780, Greece

²Department of Metallurgy, National Technical University of Athens, Athens 15780, Greece

An essential element of tunnel design is to ensure that the structural elements will not fail due to the high temperatures, which may be developed during a fire. For this problem, three different methods of passive fire protection have been developed: (a) Spraying with cementitious mortars; (b) Lining with non-combustible boards; and (c) Lining with concrete containing polypropylene fibres. However there is always a need for developing a new material with improved fire resistance properties and low cost.

The geopolymerization technology seems to be very attractive in developing effective fire resistant materials. Geopolymerization is a fast growing technology that involves a heterogeneous chemical reaction between several solid aluminosilicate materials (naturally occurring minerals, industrial by-products or waste) and alkali metal silicate solutions at highly alkaline conditions and mild temperatures. The solid aluminosilicate material slag that was used for the process of the geopolymerization was provided by the metallurgical plant of the Greek company LARCO G.M.M.S.A. that treats laterites to produce ferronickel.

Then using this slag as a raw material and a highly alkaline solution (NaOH or KOH) two different geopolymers were produced, which differ in their synthesis. The mechanical (compressive and flexural strength), physical (setting time and water absorption) and thermal properties (thermal conductivity) of the produced materials are measured and their technical data are presented. The results indicate that the produced materials have adequate mechanical, physical and thermal properties. Then, the materials are tested for their resistance under high temperatures (up to 1350 oC) according to E.F.N.A.R.C specifications and guidelines. From the tests results it is concluded that these geopolymers perform well under various fire scenarios, according to the standard fire temperature curves employed in international norms, and that may occur during a real fire incident either in a building or in a tunnel, without yielding or spalling. Also they can withstand all requirements concerning the temperature in the interface of the concrete and material. Further, it is shown that they are very cost-effective materials, taking into account that the basic raw material is a by-product not used otherwise. The cost of these geopolymers is extremely competitive compared to the existing materials used today for passive fire protection systems.

Keywords: *passive fire protection, fire resistant, geopolymers, RWS curve*

Performance Characteristics of Waste Glass Powder Substituting Portland Cement in Mortar Mixtures

Patricija Kara¹, László J Csetényi² and Adorján Borosnyói³
patricija.kara@rtu.lv

¹Department of Building Materials and Products, Institute of Materials and Structures,
Riga Technical University, Riga LV1658, Latvia

²Concrete Technology Unit, School of Engineering, Physics and Mathematics,
University of Dundee, Dundee DD1 4HN, United Kingdom

³Department of Construction Materials and Engineering Geology,
Budapest University of Technology and Economics, 1111 Budapest, Hungary

In several countries, waste glass causes environmental concerns as quantities stockpiled exceed recycling in the packaging stream. Being amorphous and having relatively high silicium and calcium contents, glass is pozzolanic or even cementitious, when finely ground. Reducing particle sizes typically to less than 100 μm may give control over the alkali-silica reaction in concrete, therefore making this material a possible substitute to Portland cement. Such use may moderate the problem of dumped waste glass and reduce CO₂ emissions into the atmosphere by decreasing the proportion of cement in unit volume of concrete produced.

In present work, soda-lime glass cullet (flint, amber, green) and special glass cullet (fluorescent lamp tube glass waste cullet and incandescent light bulb borosilicate glass waste cullet) were ground into fine powders in a laboratory planetary ball mill for 30 minutes. CEM I 42.5N Portland cement was applied in mortar mixtures, substituted with waste glass powder at levels of 20% and 30%. Characterisation and testing of waste glass powders included fineness by laser diffraction particle size analysis, specific surface area by nitrogen adsorption technique, bulk and particle density by pycnometer and chemical analysis by X-ray fluorescence spectrophotometry. Heat of hydration of cement pastes and workability of fresh mortars were also determined. Compressive and flexural strength, volume stability, early age cracking and drying shrinkage tests were performed to observe the influence of waste glass powder substitution for Portland cement on physical and engineering properties of mortar mixtures.

Keywords: *waste glass powder, cement substitution, characterisation*

Optimization of activator solution and heat curing of ground fly ash based geopolymers

Gábor Mucsi¹, Zoltán Molnár¹, Roland Szabó¹, Ádám Rácz¹, János Lakatos² and Ákos Debreczeni³
ejtmucsi@uni-miskolc.hu

¹Institute of Raw Material Preparation and Environmental Processing, University of Miskolc, Miskolc
Hungary

²Institute of Chemistry, University of Miskolc, Hungary

³Institute of Mining and Geotechnic, University of Miskolc, Hungary

Geopolymers are inorganic polymers which can be produced by the reaction between silico aluminate oxides and alkali silicates in alkaline medium. Every material are suitable for geopolymer production contains silica and alumina barrier phases, like industrial wastes; fly ash, metallurgical slag and red mud. The main disadvantage of these materials is its low reactivity which obstructs the geopolymerisation reaction.

In this paper, main process engineering properties of the raw material, such as particle size distribution, specific surface area, moisture content and density are shown. Grinding experiments were carried out by ball mill to increase specific surface area and fly ash reactivity. Systematic experimental series were carried out in order to optimize the preparation process. Fly ash with different fineness (0, 5, 10, 30, 60 minutes grinding time) was investigated to determine its optimal specific surface area. NaOH activator solution concentration also varied (6, 8, 10, 12, 14 M). Na silicate was added to NaOH as activator solution. In this serie different heat curing temperatures (30, 60, 90 °C) were also applied. The physical porperties of resulted geopolymers determined by compressive and flexural strength tests, specimen density was also measured. Furthermore the Young modulus of geopolymer was calculated. Chemical leaching tests were also carried out to determine the elements which can mobilize by different leaching solutions. It was stated that above mentioned parameters (fly ash fineness, molar concentration and composition of activator solution, heat curing) has great effect on physical and chemical properties of geopolymer specimens.

Keywords: *fly ash, geopolymer, grinding*

Corrosion-Influenced Fatigue Performance of CFRP/Steel Hybrids Using Multiple Step Test

Daniel Hülsbusch¹, Martin Klein¹, Frank Walther¹, Marion Bartsch², Joachim Hausmann²,
Meike Frantz³, Christian Lauter³, Thomas Tröster³
daniel.huelsbusch@tu-dortmund.de

¹Department of Materials Test Engineering (WPT), TU Dortmund University,
D-44227 Dortmund, Germany

²Institute of Materials Research, German Aerospace Center (DLR),
D-51147 Cologne, Germany

³Chair of Automotive Lightweight Construction (LiA), University of Paderborn,
D-33089 Paderborn, Germany

Hybrid structures provide the opportunity to design load-adapted components by complete or local CFRP strengthening and offer a high potential for lightweight construction. Such components, e.g. in automotive industry, are exposed to mechanical and environmental loads under service conditions. For a precise description and prospective prediction, in the present study the influence of pre-corrosive deterioration and in-situ salt spray load on the fatigue behavior of two hybrid structures with different steel constituents (1.0936 and 1.0332) was investigated in multiple and single step tests using in-situ strain and temperature measurements. The corrosion behavior was characterized in potentiodynamic polarization measurements and afterwards correlated with the fatigue results, yielding a process-structure-property relation for the corrosion's influence on the fatigue performance. Both hybrid structures exhibited galvanic corrosion, wherein 1.0332/CFRP combination showed significantly higher corrosion rates compared to 1.0936/CFRP leading to a worse fatigue behavior up to 78 % reduction of the number of cycles to failure observed in multiple and single step tests with pre-corroded specimens and in corrosion fatigue tests in salt spray environment. Light microscopic investigations were performed to describe macroscopic mechanical-chemical properties on microstructure basis.

Keywords: *Hybrid structures, CFRP strengthening, fatigue, multiple step test, corrosion, potentiodynamic polarization*

Structure-Oriented Fatigue Assessment of Cellulose-Based Technical Vulcanized Fiber

Bastian Penning¹, Frank Walther¹, Dominik Dumke², Bernd Künne²
bastian.penning@tu-dortmund.de

¹Department of Materials Test Engineering (WPT), TU Dortmund University,
D-44227 Dortmund, Germany

²Department of Machine Elements (ME), TU Dortmund University,
D-44227 Dortmund, Germany

Industrial production is increasingly targeting resource optimization and sustainability. In this connection, alternatives to purely oil-based plastics are sought for. The resource-friendly material vulcanized fiber is based on pure cellulose fibers leading to an unproblematic disposal at the end of the lifecycle. It is made of absorbent and unsized special papers, which are joined by a merging process into one homogenous material by adding a parchmentizing solution. After bonding, the parchmentizing solution is leached out in a multistage process by using osmotic forces.

Quasistatic and cyclic material properties of the rarely researched vulcanized fiber prove that these are comparable to those of engineering plastics. The research findings are an important basis for the reactivation of the industrial interest and the development of new applications for vulcanized fibre. In quasistatic investigations the influence of the material humidity on strength and strain properties depending on the relative humidity and the traction speed was determined and quantitatively correlated. Increasing relative humidity from 25 % to 90 % leads to a 30 % reduction of tensile strength and 5 % increased maximum strain. Increasing traction speed from 1 mm/min to 1,000 mm/min entails a doubling of Young's modulus and a 25 % higher tensile strength. Accompanying light- and electron-microscopic investigations validate the results of tensile and fatigue tests and yield a precise description of structure-property-relationship.

Keywords: *Vulcanized fiber, resource-friendly lightweight material, humidity, traction speed, quasistatic and fatigue properties*

Acoustical and thermo physical properties of metal-ceramics composites in dependence on few volume concentration of metal

Andrew Abramovich
andrew@ns2740.spb.edu

St. Petersburg State Technological University of Plant Polymers, 198092 St. Petersburg, Russia

Metal-ceramics composites (cermets) are modern construction material used in different industry branches. Their strength and heat resistance depend on elastic and thermo physical properties of cermets based on corundum and stainless steel powders which sintered in high vacuum at temperatures 1400 – 1700 °C. The volume steel concentration in the samples varies up 1 to 20 vol.%. The elastic modules were measured by ultrasonic method at room temperature, measuring of thermo conductivity coefficient were carried out at temperatures 100, 200°C by method of continued heating in adiabatic calorimeter.

We founded appearance of two extremes on dependences of elastic modules (E, G) on stainless steel concentrations, nature of which is unknown, modules values change in range: E = 110 - 310, G = 60 - 130 GPa (for different temperatures of sintering). Similar dependence is observed for thermo conductivity coefficient which values varies up 10 to 40 W/(m.K). There is presented also discussion of results based on structure cermet model as multiphase micro heterogeneous media with isotropic physical properties.

Keywords: *cermet, sintering, elastic modules, thermo conductivity coefficient*

Development of foamed Inorganic Polymeric Materials based on Perlite

Georgia-Maria Tsaousi, Iliana Douni, Maria Taxiarchou, Dimitrios Panias, and Ioannis Paspaliaris
margitsaousi@metal.ntua.gr

Department of Mining and Metallurgical Engineering, National Technical University of Athens,
15780 Zografos, Athens Greece

This paper deals with the synthesis of foamed geopolymeric boards using perlite as siliceous raw material and sodium hydroxide solution as alkaline activator. Perlite is an industrial mineral with high silicon and aluminium concentration and increased amorphous phase in its structure. The development of this new type foamed boards includes two stages : **a.** The investigation of paste's geopolymerisation and the evaluation of the paste's properties that will be important for the foaming process. **b.** The synthesis and the evaluation of the products deriving from the foaming process. The geopolymer paste is cured at temperatures from 50°C to 100 °C, while six different concentrations of NaOH solution (2, 4, 6, 8 and 10M) are also examined. In addition, the ratio solid/liquid is also studied in three different cases (1.2, 1.3 and 1.4 Kg/lit) at constant NaOH concentration. During the foaming process, hydrogen peroxide (H₂O₂) which is used as foaming agent, is added into the initial paste, studied in different percentages every time. The main purpose of this experimental set is the effect of H₂O₂ concentration on the apparent density. Five different % H₂O₂ content (0.25, 0.5, 0.75, 1, 1.25) are examined at constant NaOH concentration.

The evaluation of the properties includes the setting time test of geopolymeric pastes, the measurement of the paste's viscosity and the hydrolytic stability of the geopolymer materials. The micro-structure, apparent density and %foaming of the final foamed boards were also examined giving a representative view of this new type geopolymeric materials. Under the optimum synthesis conditions defined in this work addition the perlite based inorganic polymeric materials present setting time equal to 2.5 hours when the sodium hydroxide concentration is 2M and the curing temperature 90 °C. The pastes are viscoelastic fluids with viscosity values up to 1400cp x 10³ cp. The hydrolytic stability of solid geopolymeric structure is determined through a dissolution test in deionized water. The produced materials are quite stable in aquatic environment at low NaOH concentrations. The materials that come out from the foaming process, are porous, with satisfactory apparent density values and quite stable to water. thermal conductivity and microscopy structure perlite foam boards. It is observed that high NaOH concentration in the paste leads to higher density and lower hydrolytic stability of the final board. According to these results, the developed materials could be easily viewed as alternatives in the industrial sectors of construction and building materials.

Keywords: *geopolymers, peopolymer paste, foaming agent, foamed boards.*

The influence of the airproof composition on the thermotechnical characteristics of the enclosing structures

Mariia Platonova¹, Nikolay Vatin¹, Michael Petrichenko², Daria Nemova¹, and Issa Togo¹
nafka16@mail.ru

¹Department of Construction of Unique Buildings and Structures, Saint-Petersburg State Polytechnical University, 194064 Saint-Petersburg, Russia

²Department of Hydraulics, Saint-Petersburg State Polytechnical University, 194064 Saint-Petersburg, Russia

Air leakage leads to leakage of heat which leads to excessive energy consumption. The article contains one of the possible solutions to energy saving and energy efficiency of buildings through the use of innovative air-tight composition. It simplifies the process of air isolation. This material is durable, strong, not saturated with water, waterproof, but can miss vapor therefore it is a vapor-permeable. After the application of this composition plasterers, carpenters, tilers and electricians can work without violating the air tightness of buildings. Similarly the use of this material allows you to reach handle difficult areas. The work was tested for airtightness using this material, and without it, the sources of air leakage were examined and the results of in-place and numerical experiments were report. The advantages of use and technical indicators of composition are presented. This development will be interesting for practical application.

Keywords: *energy efficiency, energy saving, building energy saving, building materials, air permeability, external enclosure structures, innovative material*

Degradation of rubberized lean concrete

Tomasz Sadowski¹, Daniel Pietras¹
sadowski.t@gmail.com

¹Lublin University of Technology 20-618 Lublin 40 Nadbystrzycka STR, POLAND

Waste tires create big problem in the world as for their utilization. One domain in which this material is able to find promising application is civil engineering. The waste tires additive in the concrete manufacturing leads to change mechanical properties such as: Young modulus, compressive strength, fracture toughness, energy absorption, brittleness, water absorption etc. It was partly reported in the literature only for the plain concrete. There is no investigations for a lean concrete - the material -which has potential applications as a subgrade of roads.

In the first part of this paper technological aspects of the lean concrete with rubber particles was widely discussed. Preliminary numerical results under compression and bending indicate a positive influence of the rubber crumbs presence in the porous structure of the lean concrete within the elastic range. The first experimental results proved an improvement of brittleness of the considered composite.

The aim of this paper is to deliver more comprehensive results obtained during laboratory tests which allow to build up accurate numerical model of considered material in the future. In particular the laboratory tests included the investigation of the following effects like: various size of the rubber particles and their various volume fraction in the internal structure of the considered lean concrete.

The properties of the new composite materials were determined in basic tests like: cyclic uniaxial compression and cyclic bending. In order to describe gradual degradation of the rubberized lean concrete a scalar damage parameter D was introduced. The parameter is related to loading history denotes the current value of the elastic unloading modulus.

Besides determination of the damage parameter low, numerous observations of the engineering parameters such as: porosity, water absorption and thawing-freezing resistance were done. They are very important in roads engineering and serve as easy indicators of the lifetime prolongation.

Keywords: rubberized concrete, damage mechanics, waste tire

Bond performance of CFRP reinforcing bars under high loading rate at low and elevated temperatures

Adorján Borosnyói
borosnyoi.adorjan@epito.bme.hu

Budapest University of Technology and Economics, Budapest, Hungary

The mostly used bond test for reinforcing bars is the pull-out test. Carbon Fibre Reinforced Polymer (CFRP) reinforcing bars can be studied by the same method. The current testing practice usually applies static loading at room temperature for the pull-out tests. Civil engineering infrastructure elements may, however, be exposed to a wide range of service temperature and a wide range of load levels of service load.

An experimental study was completed at Budapest University of Technology and Economics (BME), Dept. of Construction Materials and Engineering Geology to study the combined influences of the temperature and rate of loading on the bond performance of CFRP reinforcing bars. Sand coated CFRP bars of 5 mm diameter were tested over a wide range of concrete compressive strength. Quartz sand and gravel was used as aggregate and CEM II/A-S 42.5 N cement was selected for the concrete mixes. Three different strength classes were targeted: one lower strength, one middle range strength and one higher strength concrete mix was designed. Targeted mean cube strengths were 30, 50 and 70 N/mm², respectively. Consistency of the fresh mixes was set by water reducing admixture to provide constant 500±20 mm flow for all mixes. Specimens were compacted by laboratory vibration table and were stored under water for 7 days and under laboratory condition up to the age of 28 days. Tests were performed on specimens of 28 days of age.

Rate of loading was applied during the pull-out tests in the possible range of service loads of concrete structures under normal service or accidental conditions as follows:

$4.63 \cdot 10^{-5}$ 1/s	$2.31 \cdot 10^{-3}$ 1/s
$1.16 \cdot 10^{-4}$ 1/s	$4.63 \cdot 10^{-3}$ 1/s
$4.63 \cdot 10^{-4}$ 1/s	$4.63 \cdot 10^{-2}$ 1/s
$1.16 \cdot 10^{-3}$ 1/s	

Temperature of the test specimens was selected as the lower and upper temperature range of concrete structures (−25 °C and 65 °C, respectively), additionally to the laboratory temperature of 20 °C. Results demonstrated that the bond strength of CFRP reinforcing bars follows the change of temperature in a more pronounced way than the compressive strength of concrete. A viscous-elastic, loading rate dependent behaviour can be realized in the bond response of the CFRP reinforcing bars. Failure of bond is realised in different mechanisms for different concrete strengths, testing temperatures and loading rates. Typical parameters of bond performance (i.e. bond stiffness, bond strength, residual bond stress) clearly show the dependence on the test parameters of which influence can be determined by the test results. The observations may foster a more refined future bond modelling of CFRP reinforcing bars that cover the influences of service temperature and loading rate. Results also demonstrated that the formulations used for the modelling of bond of conventional steel reinforcements are not optimal for the CFRP reinforcing bars studied.

A simple basic model for concrete mixtures

Gyula Pekár
alba-qualit@hdsnet.hu

Alba-Qualit Bt.
H-8000 Székesfehérvár, Kelemen Béla u. 10.

The fresh concrete mixture is a macro heterogeneous system that consists of three distinct phases: paste, which behaves in fresh concrete mixtures as a quasi-fluid dispersing agent, solid particles of aggregates, distributed in the paste as a dispersed phase, and air (void) as gaseous phase, which is present in the mixture either as a result of incomplete compaction or intentionally introduced air bubbles dispersed in the paste.

The composition of a concrete mixture with constituents of known physical properties is given by some dimensionless volume ratios (also referred to as content indicators or structural vector), i.e. volumetric proportions of paste (p), aggregate (a) and air (l) in the concrete and the ratios for the i th admixture component (α_i) of the volume of paste powder. The proportional parameters can be introduced for paste powder components also, i.e. β_k , and α_c which are respectively the volume ratios of the k th addition/cement and of cement/paste powder. At least *three* but in the most cases *five* independent content indicators necessary to describe unambiguously a certain concrete mixture with known components with known physical properties.

A series of observations at a mixing plant (Augusztin Betongyártó Kft.) and laboratory experiments (in ÉMI Nonprofit Kft.) had been carried out in the last years to find relationship between the content indicators and the performance behaviors of fresh and hardened concrete, in order to promote an effective mix design method that intends to take the influence of relatively new generations of admixtures and additions into consideration.

Factors influence compressive strength and drying shrinkage and affecting consistency was examined and some relationship was found to conclude that mixing plan observations may contribute to improve the effectiveness of concrete mix design.

In order to determine the dosage of components of the concrete mixture with a certain structural vector a material balance matrix equation was introduced. The mix composition vector (dosage of components) and the structural vector mutually define each other in a clear way, so the design of the composition of concrete mixes is possible by solving the abovementioned matrix equation.

Keywords: *concrete technology, concrete mix design, concrete composition content indicators*

Experimental Investigations and Numerical Simulations of Notch Effect in Cellular Plastic Materials

Liviu Marsavina¹, Emanoil Linul¹, Tudor Voiconi¹ and Radu Negru¹
liviu.marsavina@upt.ro

¹Department of Mechanical and Strength of Materials, University Politehnica Timisoara, Timisoara
300222, Romania

Cellular plastics are light weight structures with many applications in civil, aeronautical, automotive and mechanical engineering. Properties of cellular materials depend on the properties of the solid material, on the shape and dimensions of the cellular structure and on the relative density of the cellular material. Most of cellular plastic materials are crushing in compression and have a brittle behavior in tension. The effect of notches represents an important issue in such materials, taking into account that for packing applications for example, notches/holes should be introduced in the cellular material.

This paper investigates the effect of notches in compression for three different density 100, 145 and 300 kg/m³ polyurethane (PUR) foams. Experimental investigations were performed on rectangular blocks of 100x100x25 mm with 16, 28 and 40 mm central holes. The mechanism of damage was monitored with a High Speed Camera Photron FastCam SA 3 and with an IR camera FLIR T640.

Purpose of the numerical simulations was to calibrate a material model, based on compression test for un-notched specimens using the HYPERFOAM and CRUSHABLE FOAM models implemented in ABAQUS SIMULIA. Then the material models were used to simulate the experimental tests on notched blocks. Good agreement was obtained for the load - displacement curves obtained experimentally and from simulation. Also the plastic deformation patterns observed experimentally by IR thermography were obtained experimentally using the CRUSHABLE FOAM material model.

Keywords: *cellular plastics, PUR foams, notch, IR thermography, numerical simulation,*

Probabilistic Carbonation Assessment of the Civil Infrastructure for Future Climate Scenarios

Árpád Rózsás¹, Nauzika Kovács¹
rozsas.arpad@epito.bme.hu

¹Department of Structural Engineering, Budapest University of Technology and Economics, Budapest 1111, Hungary

This paper deals with the probabilistic assessment of the most common corrosion type of reinforced concrete structures, carbonation. This is motivated by multiple reasons: (i) concrete is the most widely used construction material Earth and reinforced concrete civil infrastructure comprises a substantial portion of the national wealth of every country. (ii) The cost of corrosion is enormous, although it is typically underestimated and overlooked. (iii) The current durability provisions are not based on reliability based calibration, but on historical data and experience. (iv) Climate change is anticipated to bring environmental changes which may accelerate the carbonation process. Considering the inherent uncertainty of the future and the driving forces of carbonation, a probabilistic approach seems to be inevitable. The aim of this paper is to investigate the effect of climate change on the carbonation of reinforced concrete civil infrastructure in a quantitative manner. For illustrative purposes the region of Carpathian Basin is chosen to carry out the calculations. Representative structures are chosen to examine the adequacy of current (Eurocode) and superseded standardized regulations. The carbonation process, the rust development and crack propagation stages are incorporated into the corrosion model. These are based on internationally accepted and experimentally verified models accounting for model uncertainty as well. The climate scenarios recommended by IPCC 2007 report are used along with a reference scenario which represents the environmental conditions without climate change. The reliability analysis is conducted using first- and second order reliability methods and simulation techniques. Beside the probability of depassivation, first crack and unacceptable crack opening, the sensitivity factors of the involved variables are also determined. The analyses show that the climate change may significantly increase the probability of depassivation and the cracking (serviceability) of civil infrastructure by the end of the 21st century. The probability of depassivation may increase by 110% for certain cement type compared to the reference scenario. The sensitivity factors give valuable insight into the processes and identify the crucial parameters which can help to alleviate the negative effects. The outcomes indicate that it would be beneficial to revise the durability regulations of the Eurocode.

Keywords: carbonation, cracking, reliability, climate change, durability, concrete

Production of lightweight fillers from recycled glass and wastepaper sludge ash

C. Spathi^{1,2}, L. Vandeperre¹, C.R. Cheeseman²
charikleia.spathi10@imperial.ac.uk

¹ Department of Materials, Imperial College London, London, SW7 2BU, UK

² Department of Civil and Environmental Engineering, Imperial College London, London, SW7 2BU, UK

The production of high-performance lightweight fillers (LWFs) has been investigated. Recycled mixed colour glass and wastepaper sludge ash (WPSA) mixes were formed into raw aggregate pellets and rapidly sintered into a rotary kiln furnace. This would represent a high value re-use application for these materials. PSA exhibits low sintering reactivity at temperatures below 1200 °C. However, milled glass powder undergoes liquid-phase sintering at temperatures where gases evolved from the decomposition of calcium carbonate present in WPSA can be encapsulated. This produces lightweight porous foamed materials suitable for use as LWFs. The effect of key process parameters such as WPSA content, particle size of the raw materials and sintering conditions (temperature and time) have been optimised. A mechanism is suggested depicting the dynamic balance between the gas escape and the inhibiting effect of liquid viscosity. Findings indicate that microstructure evolution can be described by four stages: a) heating, b) simultaneous glass softening and gas evolution, c) stabilisation and d) further densification.

Processing milled glass containing 20 wt.% PSA sintered at 800 °C for 15 minutes have a density of 1 g cm⁻³ and water absorption of 17%. The crushing strength is 2.9 MPa and this is three times higher than values for typical commercially available LWF. Therefore, there is significant potential for the artificial glass-WPSA LWFs to substitute depleting naturally sourced fillers used in construction materials.

Keywords: *Lightweight fillers; Recycled glass; Wastepaper sludge ash; Liquid phase sintering; Construction materials*

Improving the connection between wood and cement using LBL nanocoating to create a lightweight, eco-friendly structural material

Laszlo Bejo¹, Balazs Major², Zoltan Hantos³, Zsolt Karacsonyi⁴
laszlo.bejo@skk.nyme.hu

¹ Institute of Wood Based Products and Technologies, University of West Hungary

²Simonyi Karoly Faculty of Engineering, Wood Sciences and Applied Arts, University of West Hungary

³University of West Hungary, Institute of Architecture

⁴University of West Hungary, Institute of Applied Mechanics and Structures

Steel-reinforced concrete, while an excellent construction material, is heavy and very energy-intensive to produce. Replacing the steel rebars with eco-friendly natural fibre reinforcement may create a construction material that is considerably lighter, and more energy-efficient. Some wood species have been used successfully in cement-bonded wood composites, and may be used to create cement-bonded structural beams. However, preliminary experiments resulted in very low strength beams that are not suitable for construction, mostly due to the weak coupling between the wood and the cement. Layer-by-layer (LBL) nanotechnology is an innovative method that has been used successfully to improve the bonding between wood fibres and various other materials. This paper presents the results of an investigation aimed at improving the coupling between wood and cement. Poplar veneer strips were treated alternately with negatively and positively charged nanomaterial solutions, in order to make it more compatible with cement. Two different types of treatments were applied, using 10, 20 and 30 cycles of treatment in both case. After the nanocoatings were applied, specimens were planted in a portland cement matrix. Pullout tests, performed after the appropriate hydration period, showed that the treated samples required significantly higher forces to pull out of the matrix, than the untreated controls. The required pullout force increased with the number of treatment cycles. Further investigation, involving structural beams made of cement-bonded, LBL treated wood, is required to verify if this improvement is considerable enough to produce viable load-bearing elements.

Cross-laminated timber made of Hungarian raw materials

Gabor Marko, Laszlo Bejo
laszlo.bejo@skk.nyme.hu

Institute of Wood Based Products and Technologies, University of West Hungary

Cross-laminated timber (CLT), generally made out of softwood, enjoys increasing popularity throughout Europe. This material offers a versatile, eco-friendly technology to create strong, lightweight and energy-efficient buildings. Unfortunately, the sites and climatic conditions in Hungary are not suitable for growing high-quality coniferous trees. Transporting raw materials from other countries (sometimes thousands of kilometres away) negates the environmental advantages of wood-based construction. Local alternatives to imported softwood is definitely preferable from an ecological aspect.

Poplar wood (*populus* spp.) is of great economic importance in Hungary. There are several relatively large density, high strength varieties growing in large quantities in Hungary, that may be used as alternatives to softwood, with comparable properties. There is an increasing interest in using poplar as a construction material, especially in regions where there is a shortage of traditional construction timber.

Poplar has been used as a construction material, especially for roof structures, in the years following WWII in Hungary. More recently, poplar was used successfully in commercial glued structural members. However, to date, no attempt was made to use poplar in CLT. This paper presents the results of a preliminary investigation to create CLT using poplar lumber. Laboratory-scale CLT specimens were created in a hot press, and tested for their load-bearing capacity. The MOR values of poplar CLT are comparable to, albeit somewhat lower than those of softwood CLT. Further investigations are required to establish the economic viability and technological conditions for the commercial production of poplar CLT.

CFRP reinforced timber

Krisztian Andor¹, Andras Lengyel²
krisztian.andor@skk.nyme.hu

¹ÉMK, TMT, Budapest University of Technology and Economics
²SKK, MMTI, University of West Hungary

Nowadays reinforcements of old timber floor structures are usually performed using reinforced concrete, which is expensive not alone adding a significant extra load on the structure, whereas reinforcement with carbon fibre materials can increase strength adding a minimal extra weight and at a fraction of the cost of the usual concrete technology. Moreover, it may have a significant positive environmental effect for concrete is known to be one of the most environmentally hazardous construction materials due to the underlying technology of cement production. The aim of this research is the scientific analysis of compound systems of timber and carbon fibre materials that enable the reinforcement of existing timber structures or the design of new slender structures made of less wood material. The technology of reinforcing concrete structures with carbon fibre materials is known whereas its application to wood structures is yet to be developed. The most important goal is to determine experimentally the strength increase. During the research the mechanical modelling of various wood structural elements reinforced with carbon fibres will be performed in order to explore in detail the interaction of the two materials as well as laboratory experiments is be conducted to verify the analysis. It is followed by elaborating design guidelines or recommendations providing structural engineers with new tools in everyday practice that enables the application of a reinforcement system that is cheaper, simpler, and more efficient than the existing ones when reconstruction of timber floors and timber buildings or redesign due to change of function is to be performed.

Production of durable expanded perlite microspheres in a Vertical Electrical Furnace

Panagiotis M. Angelopoulos, Maria Taxiarchou, Ioannis Paspaliaris
pangelopoulos@metal.ntua.gr

Laboratory of Metallurgy, School of Mining and Metallurgical Engineering, National Technical University of Athens, Zografou Campus, Athens, Greece

Perlite is a natural occurring volcanic rock of high amorphous silica content and lower amounts of other metal oxides (Al_2O_3 , K_2O , Na_2O , Fe_2O_3 , CaO , MgO). Due to its glassy microstructure and the chemically bound water (2-6%), perlite can be expanded 4-20 times its original volume when heated rapidly at a temperature close to its softening point, namely 700-1260 °C. The initially compact, sandy-like, gray perlitic grains become (after expansion) white, frothy, lightweight with a wide network of bubbles in its index and exhibits superior insulating properties (thermal and acoustic) that renders it useful in numerous applications, especially, in the construction industry.

Conventionally, perlite expansion takes place in vertical gas-fired furnaces; the conventional perlite expansion process has certain disadvantages which affect expanded perlite products quality, thus limiting their performance and range of applications. In order to overcome the drawbacks of the conventional expansion technique, a new perlite expansion process has been designed and a vertical electrical furnace (VEF) for perlite expansion has been constructed in our laboratory. The design of the novel process enables precise control of experimental conditions in order to prescribe the furnace temperature profile and perlite grains residence time within the new heating chamber, and ensure the prevalence of milder grains heating and expansion conditions.

In the current study, fine perlite samples ($D_{p,i} < 300 \mu\text{m}$) originated from Milos Island ore mines, Greece, have been subjected to expansion in a conventional gas-fired and the novel VEF and their attained physical and mechanical properties are compared. Major conclusion of the current research study is that processing of perlite in VEF can sufficiently produce lightweight expanded perlite microspheres of limited surface porosity and significantly increased compression strength, as compared to expanded perlite samples that attained similar Loose Bulk Density and have been treated conventionally, namely in vertical gas-fired furnace.

Keywords: *expanded perlite microspheres, Vertical Electrical Furnace, durable expanded perlite, conventional perlite expansion technique, perlite properties, compression strength*

The effect of temperature and humidity on the permanence of mineral wool, EPS and XPS of ETICS applied to old story building walls

Eneli Liisma, Lembi-Merike Raado, Kristiina Tokova, Mikk Kalma
eneli.liisma@ttu.ee

Tallinn University of Technology, Building Production

According to requirements of energy efficiency of the buildings, old story house facade renovation with thermal insulation materials has been the primary focus in Northern and Central Europe in the past 10 years. Final studies have shown that facade covering solutions ensure the energy efficiency although sustainability of the facade materials having problems with durability and micro-cracks in rendering mortar. In case moisture has a direct leakage into the building through the micro-cracks, serious negative consequences will start - accelerated deterioration, dimensional changes and delamination of mortar. This study focuses on three types of plastic thermal insulation materials - expanded polystyrene; graphite enhanced polystyrene and extruded polystyrene, two types of mineral wool - stone wool and glass wool. Mineral rendering mortars were used describing the mechanism of micro-cracks. All components were tested separately and as a system of ETICS for dimensional changes and moisture content in different moisture (relative humidity from 60% to 100%) and temperature treatment (-10 C to +45 C). Tensile strength and dimensional changes of rendering mortar were tested to compare ETICS. In addition to laboratory tests in situ objects with the same materials were compared to. This paper will define the mechanism of micro-cracks in facade using different types of thermal insulation materials with mineral rendering mortar. In a conclusion technological defects in situ and unsuitability of external covering materials will be described.

The effect of fly ash addition from hard coal combustion on the fracture processes of cement concretes

Grzegorz L. Golewski¹, Tomasz Sadowski²
t.sadowski@pollub.pl

¹Department of Civil Engineering Structures, ²Department of Solid Mechanics,
^{1,2}Lublin University of Technology, Nadbystrzycka 40 str., Lublin, Poland

Nowadays, the structural concretes containing an additives of fly ash (FA) are quite commonly used in the construction industry. This is mainly due to economic reasons connected with the possibility of utilizing this industrial waste (fly ash) as an effective substitute of cement. The fly ash is probably the most frequently used pozzolanic waste materials in concrete production worldwide. Therefore they were and they are subjected of intensive research.

Many types of complex concrete defects resulted in using various theoretical micro-crack models to simulate behavior of such materials. Thus it is necessary to carry out experimental research and calculations based on I and II mode fracture.

The present study was focused on estimation of the fracture toughness in Mode I (tensile) and internal microstructure of concretes containing 0% (FA-00), 10% (FA-10), 20% (FA-20) and 30% (FA-30) volume content additive of the fly ash. Fracture toughness according to Mode I was tested in conformity with RILEM recommendations. It can be concluded that the fly ash additive changes the fracture toughness K_{Ic}^S . The optimum volume content of the fly ash, i.e. maximum increase of critical stress intensity factor K_{Ic}^S , corresponds to 17%. Concretes with the fly-ash additive ranging from 10 to 20% are characterized by high fracture toughness, while with the additive of more than 20% - low fracture toughness. The fly ash additive in the amount up to 10% slightly changes the K_{Ic}^S parameter. Similar trends in obtained results were observed when testing the same composites at the II model of cracking [1]. Also, attention should be paid to the analysis concerning the strength characteristics of the composites tested. It was observed that the concrete from batch FA-10 and FA-20 had higher compression strength than the concrete without additives.

Keywords: fly ash, concrete, fracture mechanics, Mode I fracture, cracking

Performance Evaluation of HMAC and Fibre – Reinforced Asphalt Concrete Mixes

Viktors Haritonovs¹, Janis Tihonovs¹, Martins Zaumanis¹, and Andrejs Krasnikovs²
viktors.haritonovs@rtu.lv

¹ Department of Roads and Bridges, The Institute of Transportation, Faculty of Civil, Engineering, Riga Technical University, Azenes street 16/20, Riga LV-1048, Latvia

² The Institute of Mechanics, Riga Technical University, Ezermalas street 6k, Riga, LV-1006, Latvia

Dolomite is one of the most available sedimentary rocks in the territory of Latvia. Dolomite quarries contain about 1000 million tons of this material. However, according to Latvian Road Specifications, this dolomite cannot be used for average and high intensity roads because of its low quality (mainly, LA index). Therefore, mostly imported magmatic rocks (granite, diabase, gabbro, basalt) or imported dolomite are used which makes asphalt expensive. However, practical experience shows that even with these high quality materials roads exhibit rutting, fatigue and thermal cracks. The aim of the research is to develop a high performance asphalt concrete (HMAC) and fibre – reinforced asphalt concrete for base and binder courses using only locally available aggregates. In order to achieve resistance against deformations at a high ambient temperature, a hard grade binder and polymer modified bitumen were used. HMAC workability, fatigue and thermal cracking resistance, as well as sufficient water resistance is achieved by low porosity (3-5%) and higher binder content compared to traditional asphalt mixtures. Aramide fibers Forta-Fi were used to design fatigue and thermal cracking resistant fiber – reinforced asphalt concrete. The design of the asphalt includes a combination of empirical and performance based tests, which in laboratory circumstances allow simulating traffic and environmental loads. Results are presented in the paper

Keywords: *dolomite, high modulus asphalt concrete, fibre – reinforced asphalt concrete, performance evaluation*

The Effect of Relative Humidity and CO₂ Concentration on the Early Age Properties of Reactive MgO Mortars

D.K. Panesar¹, and Y. Bilan¹
d.panesar@utoronto.ca

¹Department of Civil Engineering, University of Toronto, Toronto, Ontario, Canada, M5S 1A4

The carbonation rate of cement materials is influenced by the concentration of CO₂ and the relative humidity of the curing environment. For conventional concrete, carbonation reactions have the potential to be most prominent between 40-80% relative humidity (Chang and Chen 2006, Sisomphon and Lutz 2007, Sulapha et al. 2003). However, carbonation of reactive MgO cements requires a high relative humidity to form Mg-bearing compounds such as: nesquehonite (MgCO₃·3H₂O), dypingite (Mg₅(CO₃)₄(OH)₂·5H₂O) and arinite (Mg₂(OH)₂CO₃·3H₂O). Owing to the significant differences between the cement chemistry of conventional cement and reactive MgO, research is required to identify curing conditions under which reactive MgO pastes can achieve the greatest CO₂ uptake without compromising the physical properties and microstructure.

An experimental study is conducted to examine the behavior of reactive mortars containing up to 60% MgO under accelerated carbonation conditions. The curing carbonation chamber test conditions will consist of the same three levels of relative humidity (50, 75, and 99%) and CO₂ concentration (50, 75, and 99%). Samples will be removed from the chamber and tested at day 3, 7 and 28. The mechanical properties, microstructure, carbonation front, X-ray diffraction analysis are conducted.

Outcomes from this study will identify the correlation between curing conditions, carbonation mechanisms, the CO₂ uptake, and effects on physical properties. These results will reveal the accelerated carbonation conditions (relative humidity and CO₂ concentration) under which reactive MgO cements uptake the greatest amount of CO₂, and develop hardened properties that are equal to or exceed those of conventional cement-based materials.

Keywords: *cement based materials, carbonation curing, reactive MgO, microstructure*

is-icbm1

**The 1st International Symposium on Innovative
Carbon Based Materials**

Exfoliation of Graphite into Graphenes for Application to Transparent Electrode and Supercapacitor

Won Ho Jo, Kyung Tae Kim, Min Soo Kang and Heung-su Park
whjpoly@snu.ac.kr

Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

A high-yielding dispersion of graphene at high concentration in solvent is critical for practical applications. Herein, we demonstrate the formation of stable dispersion of pristine graphene in ethanol by exfoliating graphite flakes into individual graphene layers using a non-ionic polymer surfactant under bath-type sonication. Oligothiophene-terminated poly(ethylene glycol) was synthesized and used as a non-ionic and amphiphilic surfactant for exfoliating graphite into graphenes [1-3]. High-quality graphene film was fabricated from the exfoliated graphene solution by the vacuum filtration method. TEM and SEM reveal that the size of exfoliated graphene flake is larger than 1 μ m. When the graphene film was treated with nitric acid and thionyl chloride after washing with tetrahydrofuran, the film showed high performance with a sheet resistance of 0.3 $k\Omega \text{ sq}^{-1}$ with a transparency of 74% at 550 nm.

On the other hand, a water-soluble conducting polymer, PSSA-*g*-PANI, was also synthesized and used to directly exfoliate graphite into graphene layers in aqueous media, because PANI in PSSA-*g*-PANI is strongly physisorbed onto graphene surface via strong π - π interaction while PSSA in PSSA-*g*-PANI enhances water solubility [4]. Hence, PSSA-*g*-PANI exfoliates directly graphite into graphene layers and well disperses the layers in aqueous media, and thus PSSA-*g*-PANI/graphene composite films for supercapacitor electrode are easily fabricated by a solution process. The capacitances of the composites depend upon the length and composition of PANI in PSSA-*g*-PANI. When the capacitances of the composites with different PSSA-*g*-PANIs were measured by cyclic voltammetry, the composite with the ratio of ANI/SSA (50/50) in PSSA-*g*-PANI exhibits a very high specific capacitance of 350 F/g at a scan rate of 50 mV/s, which is among the highest values of EDLC type supercapacitor, and the composite also shows superior cycle life with 90% retention of the initial specific capacitance after 1000 cycles as compared to pseudo supercapacitor [5].

Keywords: *graphite, graphene, exfoliation, transparent electrode, supercapacitor, amphiphilic surfactant*

[1] J. U. Lee, J. Huh, K. H. Kim, C. Park and W. H. Jo, *Carbon*, **2007**, 45, 1051.

[2] J. W. Jo, J. W. Jung, J. U. Lee and W. H. Jo, *ACS Nano*, **2010**, 4, 5382.

[3] M. S. Kang, K. T. Kim, J. U. Lee and W. H. Jo, *J. Mater. Chem. C*, **2013**, 1, 1870.

[4] W. J. Bae, K. H. Kim, Y. H. Park and W. H. Jo, *Chem. Commun.*, **2003**, 2768.

[5] J. W. Jo, K. T. Kim, H. Park and W. H. Jo, in preparation.

Study of electrical and mechanical properties of silver nanowires-carbon nanofibers hybrid composites

B. Medina-Rodriguez^{1,2}, T. Castillo¹, J.M. García¹, F. Ramos¹, A. Cirera²
b.medina@fae.es

¹FAE- Francisco Albero S.A.U., Rafael Barradas 19, L'Hospitalet de Llobregat 08908, Spain

²MIND/IN2UB Electronics Department, Universitat de Barcelona. Martí i Franquès 1,
Barcelona 08028, Spain

Carbon nanofibers (CNF)-polymer materials has received great attention because of their excellent characteristics like thermal conductivity, mechanical properties, in spite of mass production. However, the electrical conductivity of CNF can be low for some applications. To overcome this drawback some studies suggest the addition of metallic materials (silver, copper,...). Thus, the aim of the present work is the development of silver nanowires (AgNW)-CNF hybrid materials showing higher conductivity, flexibility and low cost.

The main drawbacks when dealing with these hybrid materials are the lower conductivity and the higher brittleness as the polymer or silver nanowires content is higher, respectively. Therefore, the attainment of both high conductivity and good mechanical resistance has been challenging. The hybrid materials have been prepared by depositing silver-doped CNF-base pastes with different AgNW/CNF ratios by screen-printing technique. Variations in the paste composition influence substantially its processability as well as its electrical and elastic properties. The vehicle of the paste needs to guarantee stability and homogeneity as well as the appropriate flow and thickness. The solvents and additives have been optimized to obtain a paste that fits for printing.

The coatings have been characterized from a morphological (FESEM), electrical conductivity (four-point probe method) and elasticity (tensile test) point of view. Morphological analysis allowed to observe the location of both AgNW and CNF into the material. On the other hand, an increase on the electrical conductivity of the deposited films was observed after successive additions of AgNW. Finally, the elasticity was characterized detecting a decrease on the electrical conductivity when stretching. The binder percentage in the final paste composition has been optimized to achieve a loss of 10% for an elongation of 0.2.

Keywords: *silver nanowires, carbon nanofibers, hybrid materials, morphology, electrical conductivity, elasticity*

Synthesis of Carbon NanoTubes on Co, Ni, Pd Metals and Their Catalytic Activity in the Dehydrogenation of ethlybenzene

Jin Young Yang¹, Geun Woo Park¹, Geon Joong Kim^{1*}
kimgj@inha.ac.kr

¹Department of Chemical Engineering, Inha University Collegue of Engineering, Incheon 402-751, Republic of Korea

Oxidative dehydrogenation of ethylbenzene (ODE) to styrene (ST) is an attractive process due to its advantages over the conventional endothermic dehydrogenation reaction. Various catalysts such as active alumina, mixed-oxide and phosphates have been applied as catalysts for ODE, and the accumulated carbon layers deposited on the catalyst surface have been identified as the real active catalysts converting ethylbenzene (EB) to styrene. Therefore, various carbon based materials have been tested as catalysts, providing higher activity and selectivity compared to those as-stated catalysts under mild operating conditions. Among them, ODE on CNTs supported metal catalyst can be considered as a good model system. In our study, we have been involved with the study of CNTs as supports for catalytic reactions. One of the interesting features of these materials is their ability to participate in the catalytic reactions and also function as a high-surface-area support with a high thermal stability. Multi-walled carbon nanotubes (CNTs) were synthesized using Metals loaded mesoporous SBA-15 as a template under methane and carbon dioxide as carbon sources by chemical vapor deposition method. As-synthesized multi-walled carbon nanotubes were treated by NaOH at 80°C to remove the template and retain the Co, Ni and Pd metals. The multi-walled carbon nanotubes supported (Co, Ni and Pd) were used as catalysts. The Catalysts were Characterized by SEM, TEM, XRD, Raman, BET and SEM-EDX. Reaction products (EB, ST, toluene and benzene) were analyzed with a gas chromatograph equipped with FID, using a 0.32mm 30m glass column packed with HP-5. We observed various results using CNTs-supported catalysts in the dehydrogenation reaction and were expected that the Catalysts can be used efficiently for gas phase reaction. In Summary, Different contents of CNTs-supported Co, Ni and Pd catalysts were synthesized by CVD method using SBA-15 as the template under methane and carbon dioxide. The catalysts were characterized by SEM, TEM, XRD, Raman, BET and SEM-EDX. The catalytic activity was investigated for the dehydrogenation of EB at different oxidants and temperatures. CNTs-Pd (Metal 2 wt%) showed not very high activity(45.7%) but high styrene selectivity (100%) at 400°C. CNTs-Co-10 (Metal 9.5 wt%) showed the highest EB conversion (93.5%) at 700°C with a higher styrene yield (80.6). The catalysts showed a high thermal stability.

Keywords: Carbon Nanotubes (CNTs), Carbon Composite, Metal Catalyst, Dehydrogenation

Preparation of Porous Carbon Nanofibers and its Application as a Supports for Selective Adsorptive Separation of D-Amino Acids From Racemates.

Sang Gweon Jeon¹, Geun Woo Park¹, Jin Young Yang¹, Geon Joong Kim^{1*}
kimgj@inha.ac.kr

¹ Department of Chemical Engineering, Inha University College of Engineering, Incheon 402-751, Republic of Korea

In this study, Carbon Nanofibers having a pore structure were prepared and utilized as a supports for immobilization of chiral adsorbents. And then, The separation of chiral Amino Acids (AAs), by adsorption onto the heterogeneous (S)-Alanine Racemase Chiral Analogue ((S)-ARCA), was Applied using a continuous flow type packed bed reactor system. (S)-ARCA was used as an efficient adsorbent for the selective separation of optically pure D-Amino acid (D-AAs), which are industrially important as chiral building blocks for the synthesis of pharmaceutical intermediates. Porous Carbon Nanofibers (PCNFs), was prepared from a mixture of a phenolic resin and silica by the process using a electrospinning, carbonization and etc. The prepared PCNFs samples were characterized by field emission transmission electron microscopy (FE-TEM, S-4200), and field emission scanning electron microscopy (FE-SEM, JEM-2100F). The phase structure was determined by X-ray powder diffraction analysis (Phillips PW22XX and Rigaku DMAX 2500 diffractometer with CuK α ; radiation). The nitrogen adsorption/desorption analysis was performed at -196°C; by using a surface area and porosity analyzer equipment (Micromeritics, ASAP 2010). The concentration of amino acid for usability evaluation as a supports was analyzed by Alliance HPLC (Waters 2695 system) using chiral column (CH SCA(-)-51002546; 250 x 6mm), in the elluent of MeOH 60%, Water 40%, HClO₄ 5mmol with the flow rate of 1.0ml/min. The organic phase, containing (S)-ARCA adsorbent and phase transfer reagents, such as ionic liquid type molecules (Tetraphenylphosphonium chloride (TPPC), Octyltriphenylphosponium bromide (OTPPBr)), were coated on the surfaces of PCNFs supports. The effects of loading amount of ARCA on the support, the molar ratio of AA to ARCA, flow rates, and the type of phase transfer reagent (PTR) on the isolation yields and the optical purity of product D-AAs were investigated. D-AAs were selectively combined to (S)-ARCA through imine formation reaction in an aqueous basic solution of racemic D/L-AA. The (S)-ARCA coated PCNFs support showed a high selectivity, up to 95 ee%, for the separation of D-type phenylalanine, serine and tryptophan from racemic mixtures. The ionic liquids TPPC and OTPPBr exhibited superior properties to those of the ionic surfactant Cetyltrimethyl ammonium bromide (CTAB), as a PTR, showing constant optical purities of 95 ee%, with high isolation yields for five repeated reuses. The unique separation properties in this heterogeneous adsorption system should provide for an expansion of the applications of porous materials for commercial processes.

Keywords: Carbon Nanofiber(CNF), Porous Carbon, Chiral Separation, Amino acid

Synthesis of 3 Dimensionally Structured Graphene and Its Application as Supercapacitor Electrode

Geun-woo Park¹, Sang-Gweon Jeon¹, and Geon Joong Kim^{1*}
kimgj@inha.ac.kr

¹Department of Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea

Interest in graphene centres on its excellent mechanical, electrical, thermal and optical properties. There are a number of methods for generating graphene and chemically modified graphene from graphite and derivatives of graphite. The remarkable properties of graphene reported so far include high values of its fracture strength (125 GPa), thermal conductivity ($\sim 5,000 \text{ W m}^{-1}\text{K}^{-1}$) and mobility of charge carriers. Graphene and chemically modified graphene are promising candidates as components in applications such as energy-storage materials, 'paper-like' materials and polymer composites. In this study, we fabricated a 3 dimensionally structured graphene composites by using commercially available 3-grade graphene and phenol-formaldehyde(RF) sol. The RF sol was added to graphene powder, and then it was calcined in the N_2 stream after addition of sulfuric acid. The obtained graphene composite was treated KOH and calcined at $700\text{-}900^\circ\text{C}$ to form the pores in the carbon matrix. In this work, the effect of KOH amount and carbonization temperature on the pore formation was investigated. Furthermore the capacitances of samples obtained with different RF sol and graphene, KOH treatment, and carbonization temperature were compared from the Cyclic Voltametric analysis results. The graphene composite treated KOH showed a high surface area, and exhibited the very high capacitance of 150 F/g . From the instrumental analysis, the high capacitance is known to be originated due to the development of porosity in the graphene composites. The supercapacitor property of graphene composite is being studied through the loading of Mn species on it.

Keywords: Graphene, Supercapacitor, Graphene/RF Composite, Porosity

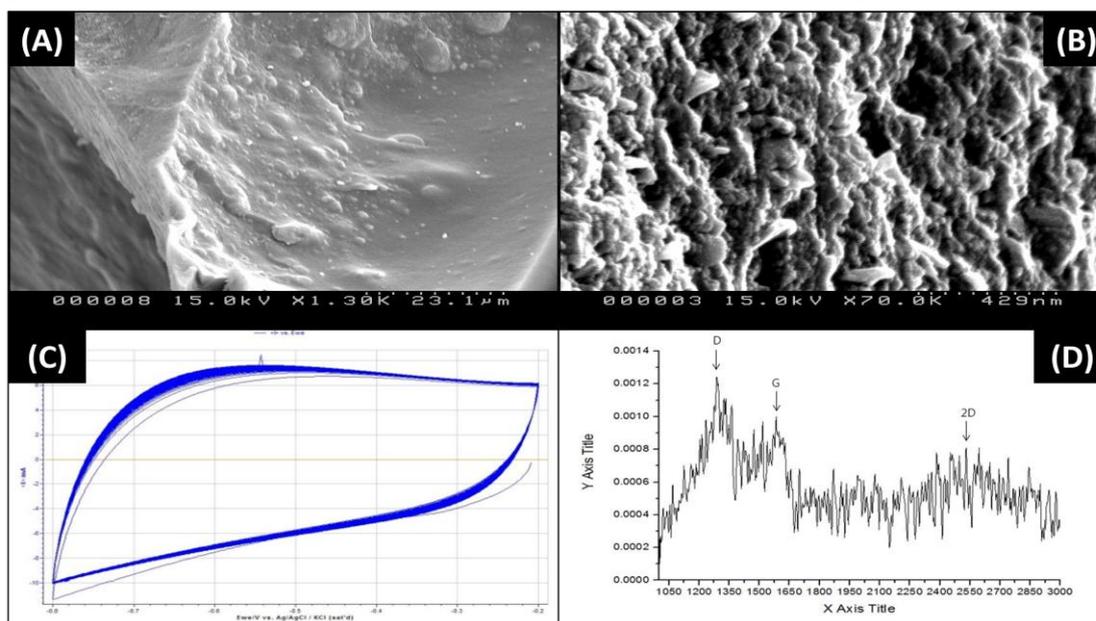


Figure (A). Fresh Graphene and RF Composite **Figure (B)** After KOH treated Graphene composite **Figure(C).** Cyclic Voltametric spectrum of KOH treated Graphene/RF composite **Figure(D).** Raman spectrum of Graphene/RF Composite

Preparation of carbon sorbents from polymeric precursors modified with acrylated kraft lignin

Magdalena Sobiesiak¹,
magdalena.sobiesiak@umcs.pl

¹Department of Polymer Chemistry, Faculty of Chemistry, Maria Curie – Skłodowska University, pl. Maria Curie-Skłodowskiej 3, 20-031 Lublin, Poland

Porous carbon sorbents are widely used for water purification purposes for removing both organic and inorganic pollutants. The main features deciding about applicability of carbon adsorbents for sorption are porous structure and surface chemistry. Both of them are formed during thermal treatment and activation process, and strongly depend on pyrolysis conditions and the nature of precursor.

Currently the interest in production of low-cost adsorbents is growing. This aim can be realized by utilization of low values by-products or residual materials as carbonaceous precursors.

Lignin is a substance that fulfill above requirements. Commercially, it is by-product of paper industry, but from chemical point of view possesses a great potential. Polyaromatic macromolecules of lignin with numerous functional groups can be equally precursors of carbon adsorbents as well as reagents in chemical syntheses of new materials.

The presented studies concern the preparation of porous carbons from a BPA.DA-St polymer containing acrylated kraft lignin as a monomer. The porous polymeric precursor in the form of microspheres was synthesized in suspension polymerization process in presence of pore forming diluents. Next weighed samples (ca. 5g) of the polymer were impregnated with acetic acid or aqueous solution of acetates (potassium or ammonia) and dried. Carbonization process was carried out in tubular furnace in nitrogen atmosphere (100mL/min.). The samples were heated from room temperature to 450°C with the rate 10deg./min. The final temperature was maintained for 30 min. The prepared porous carbons were washed with hot water and dried.

Chemical and textural properties of the porous carbon adsorbents were characterized using infrared spectroscopy, elemental and thermogravimetric analyses, and nitrogen sorption experiments.

On the surface of the studied materials oxygen functional groups are present, that is important for specific interactions during sorption processes. Additionally, after carbonization the materials remained their microspherical shape, that is desired feature for potential application in chromatography or SPE technique.

Keywords: carbonization, polymeric precursor, lignin, porous carbon, adsorbents, SPE

Fabrication and Properties of Fe Modified C/C-SiC Composites

Yuhai Lu¹, Peng Xiao¹, Zhuan Li¹
luyuhai2012@163.com

¹State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

Using needled fiber fabric as preforms, C/C preforms were fabricated by chemical vapor infiltration (CVI), then reaction melt infiltration (RMI) method was applied to manufacture Fe modified C/C-SiC composites. The microstructures, thermal diffusion coefficient, mechanical and tribological properties of Fe modified C/C-SiC composites were investigated. The results show that Fe modified C/C-SiC composites were composed of C, β -SiC and Fe_xSi_y , Fe_xSi_y included FeSi, FeSi₂, Fe₃Si and Fe₅Si₃. β -SiC grains distribute around pyrocarbon, while Fe_xSi_y phases existed between β -SiC grains. Compared with C/C-SiC composites, the thermal diffusion coefficient of Fe modified C/C-SiC composites was higher, while the compressive and flexural strength of the latter were both lower. Using 30CrMnSiVA steel as counterpart, friction coefficient and linear wear rate of Fe modified C/C-SiC composites were both higher than C/C-SiC composites, but braking curve of the former was more stable than the latter. Four different kinds of wear mechanism, e.g., abrasive wear, adhesive wear, oxidative wear and fatigue wear, exist in the tribological process.

Keywords: CVI, RMI, C/C-SiC composites, microstructure, strength, thermal diffusion, tribology, wear