

ic-cmtp2

*2nd International Conference on Competitive Materials and
Technology Processes*

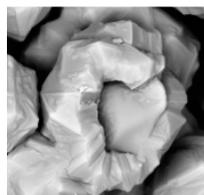
BOOK OF ABSTRACTS

2nd International Conference on Competitive Materials and
Technology Processes

Miskolc-Lillafüred, Hungary
October 8-12, 2012

BOOK OF ABSTRACTS

Edited by
László A. GÖMZE



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

PREFACE

The competitiveness is one of the most important factor in 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, chemical and biological properties and the leading companies apply more competitive equipment and technology processes.

The aims the 2nd International Conference on Competitive Materials and Technology Processes (ic-cmt2) are the following:

- 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 materials with extreme 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-cmt2, more than 250 inquires and registrations from different organizations were received. Researchers from 36 countries of Aisa, Europe, Africa, North and South America arrived to the venue of conference. Including co-authors, the research work of more than 500 scientists are presented in this book.

Prof. Dr. László A. Gömze
chair, ic-cmt2

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PLENARY LECTURES

PLENARY 1.

**Research in Competitive Materials and Technologies
in the Research Centre for Natural Sciences, Hungarian Academy of Sciences**

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The Research Centre for Natural Sciences is the biggest academic research institute in Hungary. The mission of the Centre is to carry out high level basic and applied research in different fields of science including materials science and technology, technical physics, environmental science, organic chemistry, biochemistry, medical chemistry, enzymology and cognitive neuroscience and psychology.

In this presentation we are giving a brief overview from research on advanced materials and processes in the Centre. Topics to be touched include

synthesis of nanomaterials with novel processes
research on production and application of advanced ceramics
synthesis and application of biodegradable polymers
novel polymer architectures
application of nanomaterials in sensors
nanomaterials for supercapacitors
nanomaterials for biomedical applications
processing of graphenes.

In all cases special emphasis will be taken onto correlations among composition, microstructure, macroscopic properties and synthesis and processing methods of particular materials. Possibilities for biomedical, environmental, technical and other applications will also be discussed.

PLENARY 2.

Phase Diagram as a Tool of Material Science

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Computer model of a phase diagram (PD) is becoming an important tool to investigate multicomponent system, to correct the graphics of its sections, to design the microstructures of heterogeneous material, to decipher the genotype of ceramics and alloys. As a computer model of PD saves information about system in compact form and permits to receive any projection, isotherm and isopleth with the decoding of intersected surfaces and phase regions, it helps to discover the errors and incorrectly interpreted experimental data, especially in the cases of surfaces degeneration because of negligibly small sizes of homogeneous regions.

Thermodynamic calculation doesn't guarantee an accuracy of PD in whole. E. g., in the system Au-Sb-Bi two surfaces of solidus and solvus were lost, and later they were found [1] by means of PD computer model. 3D model of PD may confirm original data, otherwise it will show the reasons for the errors.

If 3D model is formed as a set of surfaces, it may be used only to check the geometrical features of PD. If 3D model consists of phase regions, it permits to analyze the mass balances and to design the microstructures, confirming the results by mass balances: vertical ones for the given centre of masses and horizontal ones - for the isothermal states for an isopleth.

A competition of tiny eutectical crystals with more large primary crystals of the same phase in the invariant reaction with melt was investigated, and different variants of microstructures with large and small crystals and with mixed type of crystals have been located in different concentration fields.

When the phase regions are projecting on the concentration simplex, the latter is dividing into the concentration fields with the individual set of phase reactions and appropriate microstructures. Then the fields, which belong to the 3-phase regions, are dividing additionally by the surfaces of 2-phase reaction into the fragments with the different dynamics of phase masses increment. Every 3-phase region has 1-3 these surfaces of 2-phase reaction, and the sections of them are to be fixed on the isopleths and on the isothermal cuts. Analogously in the fields, connected with the invariant phase reactions, the domains with different results of the large and small crystals competition are allocated too. Like this thrice-repeated segmentation of concentrations space forms a genotype of multicomponent material [2-3].

Keywords: *concentration domains, vertical and horizontal diagrams of mass balances, competition of crystals with different dispersity, genotype of alloys and ceramics*

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PLENARY 3.

Fabrication of alkali-free resorbable and fast healing bioglass scaffolds for regenerative medicine and tissue engineering

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Bioactive glasses are a class of biomaterials which elicit a special response on their surface when in contact with biological fluids, leading to strong bonding to living tissues. In the field of bone tissue engineering (TE), bioactivity is defined as the ability of the material to bond to bone tissue via the formation of a bone-like HA layer on its surface. Due to a number of attractive properties for use in TE and regeneration, for example: enhanced angiogenesis and up-regulation of specific genes that control the osteoblast cell cycle, there is increasing effort in the use of bioactive glasses in TE applications. Since the discovery of 45S5 Bioglass®, many artificial biomaterials based on, or inspired by, Hench's glasses have been developed and successfully employed in clinical applications for repairing and replacing parts of the human body. The high dissolution rate of 45S5 glass due to its high alkali content causes fast resorption that negatively affects the balance of natural bone remodeling and in particular the physiologically vital process of angiogenesis, thus leading to gap formation between the tissue and the implant material. The alkali oxides used to lower the melting temperature might reduce the usefulness of the glass in vivo, making the bioactive glasses susceptible to water uptake by osmosis resulting in swelling and cracking of polymer matrix embedding them in composites and increase their degradation rate. High levels of alkalis degrade the sintering ability by increasing the crystallization tendency of glasses, rendering them useless for producing bioactive porous scaffolds. For example, the manufacture of porous scaffolds from the 45S5 Bioglass® is problematic owing to its poor sintering ability and a readily crystallization trend that turns this glass into an inert material with poor mechanical strength.

In the present work, a series of new glass compositions in the system Diopside – Fluorapatite – Tricalcium phosphate were prepared by the melt-quenching technique and fully characterized concerning the structure, in vitro bioactivity and degradation analysis, and thermal behaviour. The new bioglasses showed a much faster biomineralization capability, a slower degradation and smaller pH changes in comparison to the 45S5 Bioglass®. The powder frits are easily dispersed in water to form stable concentrated suspensions for colloidal processing of porous scaffolds, or dense bodies, or transformed into extrudable fine pastes that can be used for rapid manufacturing tailor made scaffolds by robocasting techniques. Full densification of the glass matrix was achieved for the novel bioglasses before the onset of crystallization, resulting in strong mechanical properties after sintering. All these features favour a strong adherence of deposited HA layer and enhance viability and cell proliferation.

Keywords: *bioactive glasses, porous scaffolds, bone regeneration, tissue engineering; robocasting*

PLENARY 4.

The 4th International Congress on Ceramics: An Examination of Emerging Opportunities in Ceramics

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The 4th International Congress on Ceramics was held in Chicago, Illinois, USA this past July. The Congress was hosted by The American Ceramic Society, under the auspices of the International Ceramic Federation. Nearly 500 business leaders and materials professionals came together to identify, discuss, and critique emerging technologies and critical areas for scientific advancement and process innovation that confront the ceramic materials community. The theme of the meeting, Shaping the Future of Ceramics, focused on ceramic challenges and opportunities in aerospace; biology and medicine; electro-, magnetic and optical ceramics and devices; environment, energy and transportation; infrastructure; nanostructured ceramics; security; and workforce development. In this presentation, the emerging opportunities identified throughout the four-day Congress will be reviewed.

Keywords: *aerospace, biomaterials, electroceramics, energy, nano-ceramics*

PLENARY 5.

Annual ICG Summer School in Montpellier – a continuing success story

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The International Commission on Glass has a wide range of activities supported by the activities of more than 20 Technical Committees, encompassing 600 participating scientists and technologists each of whom represents their country of origin. Their results are presented in an Annual Report available on an ICG web site and also at their annual conferences. Every three years these annual events are given the special status of congress and almost a thousand delegates may attend. One of these technical committees is tasked with promoting Glass Education on an international basis and a recent activity of this committee has been to organize an annual Summer School in Montpellier, France. The fourth such school was held in July 2012 with 34 participants, the target audience being new researchers. Lectures are given by international experts and include both core subject material as well as some specialist topics that change each year. A key feature is that students are divided into groups for project work and this has helped to create lasting friendships as well as innovative results. By using student accommodation for both lecturers and students, costs are kept low and opportunities for interactions are maximized. My talk will expand on the course content and explain the factors that contribute to the success of the Summer School.

Keywords: *glass, education, research students, ICG*

PLENARY 6.

Are bacteria able to synthesise kaolinite?

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Several investigations on the synthesis of hydrated aluminosilicates and on their natural occurrences have furnished important contributions to the understanding of the mechanisms controlling the formation of clay minerals. They have been viewed, for many decades, as a result of inorganic processes but more recently the role of bacteria have also been considered. As a matter of fact, there are clear evidences that bacteria may act as chemical elements attractors and microbial products have been used to develop bacterial-based heavy metals biosorbents with high affinity to target metals. Several peptides of microbial origin are able to bind aluminium that, together silicon, form the crystalline structure of clay minerals.

One of the most common clay minerals in natural environment is kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Its experimental formation at room temperature was reported for the first time by Linares and Huertas (1971; *Science*, 171, 896–897) but, despite the large number of experimental attempts by others, it was never reproduced.

In this presentation, there will be illustrated the first reported bacteria-induced experimental formation of kaolinite at room temperature (20 °C) and from Si-Al solution. The ability of bacteria to participate in the formation of clay minerals will be also reviewed.

Keywords: *kaolinite, bio-crystallization, bacteria, clay minerals.*

PLENARY 7.

Inorganic One-Dimensional Nanostructured materials

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The unique physical and chemical properties of one-dimensional materials such as nanowires, open possibilities for creating new miniature devices for various applications in electronics, optoelectronics and sensors. A large variety of materials (e.g., metal, Si, Ge, III-V, and II-VI semiconductors, oxides, and complex compound materials) have been grown in the form of nanowires using methods like chemical vapor deposition, molecular beam epitaxy or nanolithography technique. Among the huge variety of 1D nanostructures, we will restrict our focus here on the growth of Si and Ge nanowires with gold as a catalyst.

In this talk, I will first discuss the vapor-Liquid-solid (VLS) growth mechanism from a thermodynamic point of view and will point out the conditions in which nanowires can be obtained. Then I will present recent progress in realization of alignment and orientation for a massive parallel assembly of silicon nanowires, and also 3D-nanostructures trees in which the trunk of SiNW serves as the substrate for the nucleation and growth of directionally controlled branches in Ge. This later configuration has been used to explore directly the vibrational behavior of single Ge nanowires without any external manipulation such as handling, connecting or clamping that could modify the measurements of nanowire's mechanical properties. All these tailored nanostructures may find novel applications in areas ranging from nanosensors, nanoresonators infrared detectors, or using nanowires to generate electricity by harvesting energy from the environment.

Keywords: *nanowires, 1D-nanostructures, thermodynamics, VLS mechanism*

PLENARY 8.

Materials Design of Hetero-Modulus Ceramics for Extreme Environments Based on Ridge Effect Phenomenon

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The practical experience collected from the numerous tests of thermal protection systems in aerospace engineering shows that the application of monolithic as well as multi-phase ceramics, e.g. based on the refractory boride – silicon carbide systems, is very limited, because of its weak thermal-shock resistance. The only materials, which are applied currently in aerospace and rocketry practice, are carbon-carbon composites. However, all numerous attempts to improve oxidation resistance by covering the surface of these composites with various protective coatings were fruitless, because the adhesion between the coatings and substrate does not meet the necessary requirements. This general problem in the materials design for extreme environments, in particular for ultra-high temperature applications, can be solved by the replacement of carbon matrix by the high-modulus refractory carbides, such as titanium, zirconium or hafnium carbides [1], which demonstrate extremely high thermal-shock resistance and thermal strength at ultra-high temperatures, being combined with various particulate and/or fibrous low-modulus graphene-like carbon microstructures in the composite materials such as hetero-modulus ceramics [2].

The knowledge of recently discovered, temperature-pressure-dependent phenomenon termed as 'ridge effect' [3] allows preparing protective self-sintering/self-healing oxidized scales on the surface of carbide-carbon ceramic composites to inhibit considerably high-temperature corrosion/erosion of the material. The excellent adhesion of the functionally graded scales is provided by the intermediate carbon-doped oxide and oxycarbide layers [4]. By means of the pre-oxidizing technique it becomes possible to convert outer layers of the carbide matrix into oxide phases without any damage to the carbon reinforcement of hetero-modulus ceramic composites. Thus, the discovery of ridge effect becomes the milestone in the development of ultra-high temperature materials and opens new horizons for the design of the next generation of thermal protection systems in aerospace and thermo-nuclear engineering.

Keywords: *ultra-high temperature materials, refractory carbides, graphene-like carbon microstructures, hetero-modulus ceramics, ridge effect phenomenon, functionally graded materials and coatings, thermal protection systems*

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PLENARY 9.

Influence of Stratification of Mines on Tecnology and Properies of Ceramiv Roof Tiles

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After several years experiments in investigation and development of high performance technical ceramics [1, 2,] and in examination and development of hetero-modulus advanced engineering materials and ceramic matrix composites [3, 4, 5] it was an unexpected challenge to study and examine the influence of stratification of Mines on technology and properties of ceramic bricks and roof tiles. The up-to-date technology lines of ceramic brick and roof tile plants are fully automatic with high production capacities [6, 7]. The 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 clays.

In the present work are described and shown the influence of stratification of different mine layers on the followings:

- Mineral structure and composition (XRD);
- Material structure and morphology (SEM and EDAX);
- Thermo-calorimetrical properties (DTA, TG, DTG)
- Thermal dilatation and shrinkage of the conventional clay raw materials used 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: *alumina, collision, composite, diamond, dynamic, hetero-modulus, silicon-nitride, strength.*

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SESSION 1
Advanced Materials for Bio- and Medical
Applications

A Liquid Crystal Based Glutaraldehyde Sensor Using Polymer Wall as a Support Structure

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Detection of chemical and biological analytes with high sensitivity has gained considerable importance. Due to nematic liquid crystals (LC) can be used to detect molecular changes at interfaces, using the orientation order of the nematic liquid crystal (NLC) molecules in chemical and biological sensors has been extensively investigated. In general, the LC-based biosensor with high sensitivity critically requires the copper grids to confine the LC molecules and prevent the analytes to expel the LCs. However, the metal grids are expensive, unrepeatable and inconvenient. Thus, a LC-based sensor combined with the polymer wall structure, which is fabricated by the photopolymerization-induced phase separation between LC and UV-monomer on the single substrate, was proposed to replace the grids in this work. The proposed LC-based sensor is low cost, high efficiency, and reusable.

In this paper, a LC-based glutaraldehyde sensor with polymer wall structure was used to real-time and label-free detect glutaraldehyde aqueous solution. Owing to the free aldehyde group from glutaraldehyde molecule triggers the orientational transition of LC molecules, the optical response can be observed by the polarization optical microscope (POM). Different concentrations of glutaraldehyde aqueous solution (75 wt%, 50 wt% and 25 wt%) were investigated. The optical response of the reaction between glutaraldehyde aqueous solution and surface amine groups and the orientation transition of LC with exposure time was observed. The optical appearance of 75% glutaraldehyde solution was very bright, and then gradually becomes colored. Finally, it would gradually darken. The reaction time between the glutaraldehyde molecule and the surface amine groups is $t_{75\%} > t_{50\%} > t_{25\%}$. This work demonstrates the development of a simple and cost-effective LC-based glutaraldehyde sensor combined with polymer wall structure. The proposed sensing element can provide real-time sensing, fast response time (within tens of seconds), higher stability, and low cost.

Keywords: liquid crystal, photopolymerization-induced phase separation, polymer wall, biosensor

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Analysis of Benzoyl-peroxide and Formaldehyde as dental allergens by FT-SPR method

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Nowadays, the appearance of new dental materials increases as the number of induced allergic diseases. This is the origin that the more sensitive detection of allergens is of outstanding importance. The conversion of monomers to polymers is not perfect, free monomers remain in the polymer, as well as several degradation products - such as formaldehyde, benzoyl peroxide initiator, a benzoic acid derivative, etc...- are formed. The most commonly used polymer in dentistry is the polymethyl methacrylate (PMMA) which occurs from a methyl methacrylate (MMA) monomer during polymerization. The functional groups of residual MMA monomers can oxidize, what can produce formaldehyde. This small molecule is water soluble due to the enhanced reactivity of one of the most common allergens in the dental benzoyl peroxide addition. [1-2] The Fourier-Transform Surface Plasmon Resonance (FT-SPR) is a sensitive, broadly applicable real-time method for analyzing thin layers of materials on gold surfaces. SPR is conventionally performed by measuring reflectivity over a series of angles of incident light of fixed wavelength. A minimum in reflectivity occurs at the „SPR-angle,” corresponding to the maximal SPR response. SPR reflectivity measurements are surface-sensitive spectroscopic methods that can be used to characterize the thickness and refractive index of chemicals and any types of films on metal surfaces. FT-SPR measurement is performed at a fixed angle of incident light, and reflectivity is measured over a range of wavelength in the near infrared. In FT-SPR, the minimum reflectivity occurs at the „SPR wavenumber.” Since FT-IR spectrometers typically have high wavenumber resolution and precision. A wide range of reflection angles are available in FT-SPR. FT-SPR is a highly sensitive method with remarkable dynamic range for surface analysis. [3-4]

In our study we analyze the individual SPR wavenumbers of allergens, and characterize the adsorption and desorption properties of these. Resulting bonds caused by refractive index changing can be detected as shift of the resonant wavenumber which is the base of the measurements. The work/publication is supported by the TÁMOP 4.2.1/B-09/1/KONV-2010-0007 project. The project is co-financed by the European Union and the European Social Fund.

Keywords: *dentistry, allergens, Fourier-Transform Surface Plasmon Resonance (FT-SPR),*

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Binding of leachable components of polymethyl methacrylate (PMMA) and peptide on modified SPR chip

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Many types of polymers are often used in dentistry, which may cause allergic reaction (mainly methyl methacrylate allergy) due to the leachable, degradable components [1-3] from polymerized product. The aim of this study was to investigate interactions between leachable components (formaldehyde, methacrylic acid) and peptides by Fourier-transform Surface Plasmon Resonance (FT SPR).

In our previous work binding of oligopeptides (Ph.D.-7 and Ph.D.-12 Peptide Library Kit, Biolabs, New England) was investigated to PMMA (Orthocyl, Dentaureum, Germany) surface by phage display technique. It was found that amino acids of peptide library were bound specifically to polymer surface and among the PMMA-specific sequences the most frequent amino acids were proline (Pro) and leucine (Leu). For the analysis of binding amino acids and leachable components were used a SPR 100 (Thermo Electron Corp., Waltham, MA, USA) module equipped with Nicolet 6700 FT-IR (Thermo Electron Corp., Waltham, MA, USA). The SPR chip was modified using alkane thiol to generate a self-assembled monolayer (SAM) on the Au chip surface in favor of specific binding between peptide and leachable components. The thiol formed a bond with the gold surface while the other end of the molecule provided a functional group for the amino acids. The free functional group of amino acids attached to degradable chemicals. At each binding the SPR sign shifted on the reflectance (%) - wavenumbers (cm⁻¹) curve by indicating the specific binding on the chip surface.

By the application of phage display and SPR modern bioanalytical methods those specific binding peptide sequences can be analyzed which may occur in that haptens or immune mediators that can be responsible for allergic reaction. The work/publication is supported by the TÁMOP 4.2.1/B-09/1/KONV-2010-0007 project. The project is co-financed by the European Union and the European Social Fund.

Keywords: *phage display, dental allergy, FT SPR, surface modification*

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Characterization of Nanobiomaterials

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Nowadays the medical applications of different nanoscale (10^{-9} - 10^{-6} m) materials are in the focus of interest in therapy as well as diagnosis. These small particles have unique properties, mainly due to their nanometer sized range and high surface area/volume ratio. This special ratio results in the location of higher proportion of atoms on the surface which means more adsorption capacity and more biological effects.

In our work different types of nanomaterials were studied. We focused on liposomes and functionalized carbon nanotubes as possible drug delivery systems. Particles size was measured using dynamic light scattering (DLS) by Zetasizer Nano-ZS. This technique measures the time-dependent fluctuations in the intensity of scattered light which occur because the particles are undergoing Brownian motion. Analysis of these intensity fluctuations enables the determination of the diffusion coefficients of the particles which are converted into size distribution. The mean count rate (average number of photons detected per second) reflects changes in the optical properties of the material during temperature variations. This method allowed to specify the phase transition temperature of different lipid containing liposomes. Functionalized (-OH, -COOH) carbon nanotubes (CNT) were measured in different media. Size dependence of CNTs was examined in water, phosphate buffer saline (PBS) and in human plasma.

Size characterization of nanobiomaterials is essential as their biological behavior is strongly dependent of the size.

Keywords: *nanomaterials, liposomes, functionalized carbon nanotube, light scattering, size, and phase transition temperature*

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Crystallization process of a biomaterial, the lithium disilicate, obtained from rice husk silica

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Lithium disilicate is an important biomaterial for dental application, it is a commercial product, frequently used as prosthesis, but just produced using SiO₂ from commercial source, these work investigated the crystallization process of lithium disilicate glass-ceramic with SiO₂ from rice husk silica replacing the high-purity SiO₂ starting powder from commercial source. Glasses were developed at the stoichiometric composition of 66%.molSiO₂:33%.molLiO₂ using commercial SiO₂ and the one obtained by thermochemical treatment of rice husk. To compare the SiO₂ sources, the influence of the one from rice husk on crystallization process was measured using different granulometry, analyzing microstructure and the kinetic behavior. Investigations were carried out by means of differential thermal analysis (DTA), X-ray fluorescence (XRF), X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Amorphous glasses were obtained after melting using a bronze mold. The position of lithium disilicate glass-ceramic crystallization peaks (Tp) are between 550 to 660°C to different granulometry (<63µm, 63µm < x < 250µm and 1mm < x < 2mm) and DTA heat rates (5; 10; 15; and 20°C/min) in both glasses, and the relevant formed crystalline phase after DTA analysis (verified for XRD) was Li₂Si₂O₅. Mechanical properties were determined by Vickers Hardness for amorphous and crystalline (with different temperatures of heat treatment, based on DTA results and literature) materials. SEM images showed the increase of glass substitution for crystalline phase to both glass-ceramics from different silica sources.

Keywords: *bioceramic, lithium disilicate, prosthesis, rice husk silica, dental, thermal analysis*

Deformation Behavior of Porous Ceramics for Medicine

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It has been studied a porous ceramics obtained from nanocrystalline ZrO₂ powders. Samples were obtained by pressing and sintering of compacts, the porosity of ceramic samples was from 20 to 80%. The average grain size in the studied ceramics increased from 0.4 to 4 microns with increasing sintering temperature and duration of isothermal holding from 1400 to 1600 0 C and 1 to 5 hours, respectively.

It was shown that the “stress - strain” diagrams are not typical for brittle materials - the stage of active deformation begins with part which is characterized by a nonlinear relationship between stress and strain. The fracture of the materials was observed from the elastic area.

It was shown that during decreasing the porosity in the ceramics - the tensile strength and a modulus of elasticity were increased from 50 to 1200 MPa and from 5 to 80 GPa, respectively.

It was shown that when a decrease in the porosity in the ceramics the value of the deformation of the corresponding of the beginning of fracture was increased on from 0.2 to 4.5%.

Effect of sintering process parameters on the properties of 3Y-PSZ ceramic

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The effect of sintering process parameters on the properties of 3 mol% Y_2O_3 partially stabilized zirconia (3Y-PSZ) ceramics have been investigated. The relative density of the sintered pellet rapidly increases from 70.5% to 93.6% with temperature increased from 1473 to 1573 K. Moreover, the relative density only increases from 93.6% to 96.6% when sintered temperature from 1573 to 1773 K. This result indicates that no significant influence on the densification behavior when sintering at 1573 to 1773 K for 2h. The Vickers hardness and toughness also increase with the sintered temperature. The densification of 3Y-PSZ sintered ceramics is achieved by the shrinkage of the open pores and the grain boundary diffusion.

Keywords: *Sintering process, 3Y-PSZ ceramic, Relative density, Vickers hardness, Toughness*

Effects of Magnesium Ions on Proliferation and Differentiation of Human Bone Marrow Stroma Cells

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Recently, magnesium (Mg) has been proposed as a bone implant biomaterial due to their biodegradability and good mechanical properties. We investigated the effects of Mg ions on proliferation and osteoblastic differentiation of human bone marrow stromal cells (hBMSC) and whether the CaR and Wnt/ β -catenin signaling is involved in this mechanism or not. We isolated BMSC from human bone marrow aspirated from femur medullary canal during hip joint arthroplasty with informed consent. To evaluate the effects of Mg ions on osteoblastic differentiation of hBMSC, we examined the difference among the groups with Mg chloride, Ca chloride, Sr chloride and control by measuring the hBMSC proliferation, alkaline phosphatase (ALP) activity. Proliferation was evaluated by WST method with a cell-counting kit and ALP activity was determined using p-nitrophenyl phosphate as the substrate. Then we analyzed mRNA expression of osteogenic-related genes, including ALP and osteocalcin (OCN), and CaR, using RT-PCR. Next, we examined the effects of CaR inhibitor, calhex231, on that of hBMSC to determine whether CaR may impact on Mg-induced proliferation of hBMSC. Finally, to confirm the effects of Mg on Wnt signaling, we analyzed the protein expression of β -catenin by Western Blot analysis. β -catenin, the pivotal protein in the Wnt signaling, was also observed by immunofluorescence analysis for nuclear translocation. hBMSC proliferation during 48h, 72h was significantly increased in Mg ($p<0.05$ and $p<0.05$), Ca ($p<0.01$ and $p<0.001$), and Sr ($p<0.05$ and $p<0.001$) groups comparing with the control group. Treatment of hBMSC with Mg for 14 days also enhanced ALP activities similar to Sr-treated cells ($p<0.001$). In addition, both ALP and OCN mRNA levels were tended to be increased by Mg treatment. Mg also increased the mRNA expression of CaR. Interestingly, 24h pre-treatments of the cells with calhex231, a CaR inhibitor, significantly and almost totally antagonized Mg-induced proliferation of hBMSC ($p<0.001$). Moreover, Western Blot analysis showed that Mg increased β -catenin levels in the nucleus, confirming the results obtained by immunofluorescence analysis. Increase of β -catenin in the nucleus may promote the transcriptional activity. This study demonstrated that Mg can promote proliferation and osteoblastic differentiation of hBMSC. Although further studies seem to be necessary, this effect is, at least partly, mediated through the activation of CaR and wnt/ β -catenin signaling. Therefore, this might provide the possibility of magnesium for the treatment agents of osteoporosis and of using the magnesium metal as bone implant biomaterial.

Electrospun nanofibers of PVP based Sodium Cobaltite

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Cobaltite of sodium, embedded in Poly Vinyl Pyrrolidone (PVP) polymeric fibers forming nanocomposite were synthesized by combining conventional process route of sol-gel with electrospinning method. Ultrathin diameter polymer fibers containing nano regime ceramic particles, by varying various process parameters like voltage, concentration, feed rate, distance between nozzle tip and base plate etc. to reach optimized results in each case to get ultrathin nanofibers and ceramic particles embedded in it. Characterization was done to verify the synthesis parameter effect on structural and surface morphology of polymer based nanofiber composite. X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) was used as tools for structure verification and study of structural morphology and its correlation with process parameters. Atomic Force Microscopy (AFM) was done for better characterization. These fibers are potential candidates for their use as thermoelectric materials and that has also been investigated.

Glucose oxidase self-encapsulated within polypyrrole research in fluorescence spectroscopy

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Glucose oxidase (GOx) has a great interest because of its wide application in bioanalytical chemistry, biomedicine and biosensors industry. The enzyme biosensors in nanotechnology are a widely investigated area and have many different methods of enzyme immobilization with GOx for constructing biosensors. When composing these biosensors most important characteristics are stability, sensitivity, biocompatibility, selectivity and the possibility of miniaturization. Immobilization matrix should provide stability and activity for immobilized enzyme. From these points of view, the polypyrrole (Ppy) could be very suitable as the immobilization matrix.

Free enzymes are usually not stable and therefore their application in sensing system is complicated. Immobilized enzymes exhibit better stability and longevity than free enzymes in solution [1]. Glucose oxidase self-encapsulation within polypyrrole was achieved and this process was monitored by the registration of flavin adenine dinucleotide (FAD) auto fluorescence spectra at different periods. Not encapsulated enzyme's fluorescence was measured and compared as well. In this work presented data shows that at the same environmental conditions the glucose oxidase if encapsulated within polypyrrole is more stable in comparison with native enzyme.

Unfolding of GOx from *Penicillium vitale* was investigated by monitoring the fluorescence of cofactor FAD. During denaturation of the GOx, FAD dissociated from the enzyme, which was clearly reflected in fluorescence spectra. The GOx was coated by polypyrrole shell (GOx/Ppy nanoparticles). The ability of Ppy to decrease unfolding process of enzyme was investigated. The stability of the GOx encapsulated within Ppy was observed by the FAD fluorescence measurements.

Key words: *Glucose oxidase, photoluminescence, polypyrrole, conducting polymers, encapsulation.*

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Hydroxyapatite/poly (lactic acid) hybrid microparticles as building blocks for additive technology.

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Calcium phosphate (CaP) bioceramic is well known as bioactive and biocompatible material in bone tissue regeneration applications. Apatitic CaP (ap-CaP) is more similar to the natural apatite present in bone tissue than CaP bioceramic. In the current research ap-CaP was modified using biodegradable polymer poly (lactic acid) to increase the mechanical strength of ap-CaP and to decrease its bioresorption rate. Prepared hybrid materials could be the potential candidates for the scaffold preparation using additive technology.

Apatitic CaP was synthesized by wet precipitation reaction between calcium hydroxide and phosphoric acid. Hydroxyapatite/poly (lactic acid) (HAp/PLA) hybrid microparticles were fabricated using solid-in-water-in-oil-in-water ($S/W_1/O/W_2$) method. Dichloromethane was applied as organic phase solvent and polyvinyl alcohol was used as $S/W_1/O/W_2$ system stabilizer. SEM investigations were performed to evaluate the microparticle surface morphology and inner structure and light microscopy was used for characterization of the microparticle form, particle size distribution, as well as for detection of agglomerates.

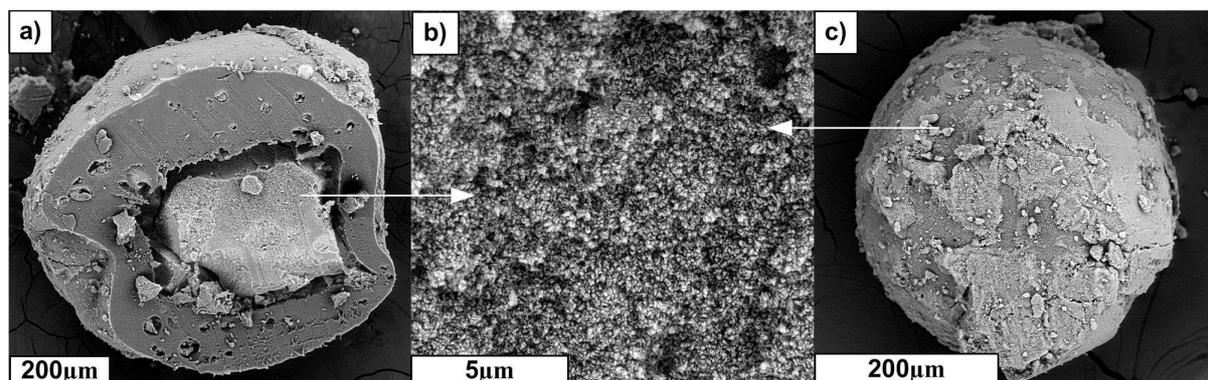


Figure 1. SEM microphotographs of HAp/PLA hybrid microparticles: a) cross-section; b) nanosized hydroxyapatite; c) surface morphology.

Results showed that $S/W_1/O/W_2$ method is suitable for the preparation of HAp/PLA hybrid microparticles covered with nanosized HAp crystals. Depending on the volume of W_1 phase, single domain or multi-domain microcapsules with different surface morphologies can be obtained. Encapsulation efficiency of ap-CaP strongly depends on the microencapsulation process parameters used (volume of w_1 phase and amount of w_2 phase).

Keywords: *Microparticles, apatitic calcium phosphates, poly (lactic acid), emulsion stability, microencapsulation*

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Hydrothermal degradation of 3Y-TZP zirconia ceramic with ternary and quaternary oxide additions

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Yttria stabilised tetragonal zirconia polycrystal (Y-TZP) ceramics have attracted particular attention due to their outstanding mechanical properties. However, many potential engineering applications for Y-TZP ceramics are currently limited as a consequence of a catastrophic degradation of their strength due to hydrothermal degradation. Hydrothermal degradation is the autocatalytic transformation of the metastable tetragonal (*t*-ZrO₂) to the equilibrium monoclinic (*m*-ZrO₂) at a free surface held in a moist atmosphere at elevated temperature (typically 100-600°C). The underlying cause of this degradation process is still a matter of considerable debate and many attempts to improve the resistance of Y-TZPs to hydrothermal degradation have generally resulted in an unacceptable loss in toughness. The most prominent case where hydrothermal degradation has had a major negative consequences was associated with the failure of zirconia used as femoral heads in hip prosthetics. In the current work, the hydrothermal degradation of a 3Y-TZP with and without small additions of Al₂O₃ and La₂O₃ was investigated at 134°C in superheated steam. This temperature was chosen as it is believed that one hour in the superheated steam represents one year in vivo. Ceramics were prepared by conventional methods using milling the oxide powders in the appropriate proportions, isostatic pressing followed by sintering. Sintering conditions were chosen to ensure that the same grain size and indentation fracture toughness were achieved in all materials, which were close to theoretical density. TEM of sintered materials demonstrated that the ternary oxide additions segregated to grain boundaries. Prior to degradation the surfaces were prepared by careful polishing to produce an extremely flat surface, followed by thermal etching to minimise residual surface strains and to ensure the starting surface was fully tetragonal zirconia. Early stages of degradation were followed by atomic force microscopy while the overall kinetics was quantified through X-ray diffraction and measurement of the transformation depth using surface cross-sections. Materials with ternary oxide additions exhibited superior degradation resistance to the base zirconia material. In addition, the mechanism of degradation appeared to be fundamentally different. The relationship between degradation rate and composition is discussed.

Influence of particle/agglomerate size on injectability of tricalcium phosphate bone cement pastes

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The research and development of calcium phosphate bone cements (CPC) with mechanical properties suitable for bone graft applications in the most demanding surgical procedures, such as vertebroplasty and kyphoplasty, have attracted much attention in the last years. However, the injectability of CPC is still far from being satisfactory. The flow properties of CPC pastes depend on a number of factors such as particle size (PS) and particle size distribution (PSD), nature of the phases presented (amorphous or crystalline), liquid-to-powder ratio (LPR), the presence of additives, etc.. The effects of the presence of particle agglomerates on injectability are still far from being well understood. Therefore, the present study aims at investigating the influence of PS, PSD of β -tricalcium phosphate (β -TCP) powders and of the presence of controlled amounts of different sized spherical agglomerates on the rheological properties (flow curves and injectability) of non-reactive systems.

β -TCP powder was prepared by an aqueous precipitation method from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ salts. The precipitated powder was separated by filtration, dried and calcined at 800°C, 900°C, 1000°C and 1100°C. The calcined powders were dry milled for different times (0, 6 and 12 minutes) to obtain β -TCP powders with different particle/agglomerate sizes and particle/agglomerate size distributions. Spherical granules of β -TCP were then prepared from a well dispersed suspension sprayed into liquid nitrogen followed by freeze-drying and sintering up to near full density, sieved and separated by sizes. The characteristics of β -TCP powders and granules were assessed by measuring size distribution, BET specific surface area, scanning electron microscopy (SEM) observations, and X-ray diffraction (XRD). Full dense β -TCP spherical granules could be obtained by sintering at a temperature below that of β -TCP to α -TCP phase transformation so as to simulate uniform particles.

The results collected along this work shed further light on how some specific characteristics of starting powders resulting from their thermal and process history, such as the specific surface area, morphology, and state of agglomeration affect the flow properties of the pastes prepared thereof.

Keywords: *calcium phosphate, bone cement, injectability, agglomeration state, particle size*

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In vivo implantation of new porous ceramic granules

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Study Background. Bone defect replacement with biomaterials allows avoiding adverse effects related to bone graft harvesting and application [4]. A range of porous bioceramics are the most promising materials for bone replacement. Their principal advantage over other materials (metals and polymers) is their excellent biocompatibility [1]. Effective restoration of bone defects in fractured vertebral bodies requires application of artificial bone substitutes with sufficient strength and porosity. Mechanical properties of currently used materials, such as calcium phosphate ceramics, bioglass, and glass ceramics, are inadequate [2, 3]. Therefore the search for materials with superior properties is very urgent.

Materials and Methods. Randomized prospective blinded study was designed, and an experimental implantation of porous ceramic granules to the lumbar vertebral body and femoral diaphysis of 24 Kyoto-Wistar rats aged 10 months was performed. Animals were divided into three groups: 1) rats with implanted bioceramic granules (specimens No.1) 2-3 mm in size, with a predominant pore size of 50 microns and compressive strength of not less than 70 MPa (n = 8); 2) rats with implanted bioceramic granules (specimens No.2) 2-3 mm in size, with a predominant pore size of 200-400 microns and compressive strength of not less than 50 MPa (n = 8); and 3) rats with implanted bioceramic cylinders (specimens No.3) 1000 microns in diameter, with through pore about 500 microns in diameter and compressive strength of not less than 300 MPa (n = 8). Implantations were performed under sterile operating room conditions into the lumbar vertebrae and femurs of animals with pre-modeled bone defects having sizes exceeding those of bioceramic granules. Animals were sacrificed two months after surgery. Zone of implantation was resected en block with surrounding tissues. Specimens were fixed in epoxy resin and studied under electron microscope Carl Zeiss EVO 50 XVP (accelerating voltage 5 kV). Chemical analysis was performed using INCA Energy Dispersive Spectrometer.

Results. The experiment showed that osseointegration of bioceramic granules occurs 2 months after their implantation. Pores in specimens No.1 mostly have no connections between each other. There is no tissue ingrowth into bioceramic granules in these specimens. Mean pore diameter in specimens No.2 varies between 200 and 400 microns, though total porosity is below the required value. Ingrowth of connective tissue is observed here. In specimens No.3 the ingrowth of compact bone tissue into pores is noted.

Conclusion. Findings of electron microscopy and energy dispersive spectral analysis suggest that new porous bioceramic granules possess osseointegration ability what indicates that they have a promising use as an effective osteoplastic material.

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Is the ubiquitous presence of barium carbonate responsible for the poor aqueous processing ability of barium titanate?

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The ubiquitous presence of barium carbonate (BaCO_3 – BC) as an impurity in barium titanate (BaTiO_3 – BT) has been pointed out as the main reason for the well-known difficulties found by many investigators when attempting to process BT powders in aqueous media. Different and controversial arguments have been put forward to justify the observed aqueous processing difficulties of BT, but a satisfactory explanation is still to be found. Therefore, before embarking in the BT boat, it seems advisable to firstly study and understand the solid/liquid interactions occurring at the surface of BC and its ability to form concentrated dispersions. In this work colloidal stable aqueous suspensions of barium carbonate with solid loadings as high as 60 vol.% and good flow behaviour kept along extend time periods could be easily prepared. This proves that the intrinsic instability of BT particles in contact with water cannot be attributed to the presence of BaCO_3 as an impurity. Hints for a better understanding and control the aqueous processing of BT powders are given

Keywords: *Barium carbonate; Barium titanate; Dissolution; Dispersion; Aqueous processing*

Layered Porous Materials of Gelatin and β -Tricalcium Phosphate for New Bone Regeneration

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The calcium phosphates have been investigated as tissue engineering scaffold in bone defect area. However, the brittleness of calcium phosphate scaffold was considered as disadvantage for its use as implant materials. Hence, to enhance the mechanical properties of calcium phosphate scaffolds, some of the biocompatible polymer coating was used, while the macropores interconnectivity was maintained. Also, the micropores on the surface of scaffold are expected to enhance the active oxygen diffusion that resulted in better biological properties than those with smooth surface.

In this study, multi-porous β -tricalcium phosphate (β -TCP) scaffolds were fabricated using various porogen followed by gelatin coating to make them flexible and machinable.

Paraffin bead and polyurethane sponge were used as templates in template-casting method and sponge method. For the sponge methods, β -TCP slurry was prepared by dispersing the prepared β -TCP powder into distilled water with binder, dispersant and drying chemical control additive, respectively. Following the sponge coating, the samples were sintered at 1250°C for 3h to densify the β -TCP scaffolds. The gelatin slurry was prepared by mixing of gelatin and distilled water. After the dip-coating method, the scaffold was dried at 50°C for 3h. The control samples were prepared by forming the scaffolds without gelatin slurry dipping. The fabricated samples were characterized by evaluating their surface morphologies using the scanning electron microscopy (SEM) and their compressive strength was determined by a universal testing machine (UTM). The cell proliferation and differentiation were measured by cell counting assay and gene expression.

The scaffold coated by gelatin was shown to be better in mechanical properties than the control. The scaffold with multi-pores and gelatin coating showed enhanced cell adhesion, proliferation and differentiation. The multi-pores enhanced the biological properties due to the high oxygen diffusion on their surface and the gelatin coating of scaffold enhanced the mechanical properties.

The gelatin coating of multi-porous scaffold showed the enhanced mechanical and biological properties, suggesting its potential application as the implant material.

Nanostructured Ceramic Materials for Traumatology and Orthopedics Applications

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CJSC “NEVZ-CERAMICS” in collaboration with Institute of Metallurgy and material Engineering, RAS developed a technology of production high- and ultra-disperse powders of oxide composites for medical use with the sol-gel method, this technology involves organic complex formations (precipitators) used in the composition of the reaction mixture.

The powders were pressed with ultrasound oscillations (method of O. L. Khasanov, Tomsk). Thus the decrease of the average size of grains by 54 % and average size of pores by 36 % compared to regular ceramics was attained.

After thermal treatment the nanocomposite implants are subject to finishing HIP this makes possible to attain density of 99% of the material's theoretical density thus we produce implants of high-density ceramics with high values of flexural strength and considerably decreased wear rate.

The problem of increasing osteoplastic activity of the porous implants is solved by applying hydroxyapatite formed with use of the mechanosynthesis method. This method allowed us to synthesize nano-crystalline hydroxyapatite with a certain composition of granules within a short period of time and without further sintering. The studies were carried out based on the technology developed in the Institute of Chemistry of Solid States and Mechanochemistry, Siberian Division of Russian Academy of Science. Magnetron methods for applying coating of this material to the surface of the porous ceramics allow one to achieve effect of submicron film “lining” while pores remain open for biological substrates that contact the implant.

The sequence and methods of forming ceramics nanostructural composites and coatings form a base launching a technology of industrial production of high-quality ceramics for traumatology and orthopedics.

Results of the toxicological tests according to ISO10993 show that the developed ceramics materials are non toxic when used under condition of their application.

Observation of cellular uptake behavior of layered double hydroxide nanoparticles possessing visualization probe characteristics

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Inorganic materials, such as layered double hydroxide (LDH), hydroxyapatite, carbon nanohorn, quantum dots, etc., are increasingly used in medical or biological applications, such as bioimaging, diagnostic technology and drug/gene delivery. Recently, the synthesis and cellular uptake of biomolecule intercalated LDH have been reported. The uptake was considered to proceed by the endocytosis, however, the uptake mechanism has not been clarified in detail. In order to reveal the cellular uptake behavior of biomolecule intercalated LDH, a fluorescein (Fluo) intercalated LDH (Fluo/LDH) was synthesized and the cellular uptake behavior of the Fluo/LDH was observed by microscopy.

The Fluo/LDH has been synthesized by coprecipitation and hydrothermal methods. The XRD patterns showed that the Fluo/LDH has a LDH structure possessing the d003 of 0.77 nm. Although the Fluo content in the Fluo/LDH is very low, the clear green fluorescence was observed from the Fluo/LDH by the fluorescence microscope observation. Moreover, the Fluo/LDH and Fluo exhibited very low cytotoxicity as a result of the colony formation assay. These results indicated that the Fluo/LDH can be used as an intracellular fluorescence probe. The cellular uptake of the Fluo/LDH in mammalian cell lines (L929) has been investigated. The intracellular fluorescence of the Fluo/LDH was observed using a confocal laser fluorescence microscope. Although the intracellular fluorescence was not observed when unsupported Fluo was used, the Fluo/LDH treated cells showed intense fluorescence in the cytoplasm. TEM photographs of the cellular section demonstrated that the Fluo/LDH was internalized to L929 cell by endocytosis. Obviously, the Fluo/LDH was uptaken in endosomes within 10 min of incubation time. This means that endosome formation rate was very quick. Therefore, highly dispersed LDH nanoparticles can be expected to be prone on the plasma membrane periphery to be uptaken into the cell efficiently.

Keywords: *layered double hydroxide, fluorescein, cell, cellular uptake, endocytosis*

Acknowledgment:

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Processing and Properties of Bio-Ceramics Based on Oxides Nanopowders

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The objects of investigation were ZrO₂ ceramic samples, their porosity ranged between 2 and 60%. It was shown that during mechanical activation zirconia-based nanosystem was divided into two subsystems with the average size of structural elements differing by two orders of magnitude. The fraction of the quasi-amorphous (X-ray amorphous) phase therewith increases. In this ceramics during sintering were formed rod-like structures with a high macro-deformation, which was realized as quasi-elastic area due to micromechanical instability in matrix under deformation. In this case, the attainable strain and ultimate stress of ceramics produced from such powders greatly exceed the values for coarse-grained ceramics with similar parameters of the porous structure. It was shown that microdamage accumulation has a threshold character and after local fracture the material is deformed by the previous law. There is direct correlation between macrostresses and local (meso-) parameters of strain distribution. The regions of uniform strain accumulation alternate with the regions where strains change abruptly, which leads first to local and then to macrofracture of the entire material. It has been found out also the correlation between the sizes of crystallites, fractal dimension, and porosity, which associated with transition of the isolated porous structure to the continuous one and the porosity of 20%, corresponds to the first percolation threshold.

It was shown that these sintered porous ceramics has very similar mechanical properties and morphology structure as compare natural bone.

Properties of novel hemostat prepared using calcium-deficient hydroxyapatite, phosphoryl oligosaccharides of calcium and thermoplastic resin

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A novel hemostatic agent was prepared using a sugar modified calcium-deficient hydroxyapatite ($\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x} \cdot n\text{H}_2\text{O}$ ($0 \leq x < 1.0$); sHAp), phosphoryl oligosaccharides of calcium (POs-Ca) and thermoplastic resin (random copolymer of ethylene oxide and propylene oxide adding polymer of ethylene oxide; 25EPO-15EO). The releasing behaviors of gentamicin sulfate from the hemostats containing sHAp, POs-Ca and 25EPO-15EO were examined in the presence of phosphate buffer saline. To evaluate biocompatibility, Vellanueva bone stain were evaluated by hemostats implantation of tibia and femur of Japanese white rabbit. The commercial 25EPO-15EO was mixed with de-ionized water to form a gel (25EPO-15EO to de-ionized water=0.20 (in mass)). Then the gel was flash frozen at -80°C , freeze-dried at -50°C for 15 h, and sieved to obtain the 25EPO-15EO powder with the sizes of 1 to 2 mm. The resulting 25EPO-15EO was further blended with sHAp (Ca/P ratio: 1.56), which had been prepared by the hydrothermal heating of POs-Ca solution at 100°C for 5 h. Then the de-ionized water was put into the blended powder to form the 25EPO-15EO gel with sHAp addition. The resulting sHAp consisted of 60.5 % hydroxyapatite and 39.5% organic materials. The hemostatic agents, whose consistencies had been adjusted to be 18 mm (*i.e.*, the consistency of commercial agent) by using the de-ionized water, possessed the stanching times of 5.3 h (pure 25EPO-15EO), 4.7 h (POs-Ca/25EPO-15EO composite), and 8.2 h (sHAp/25EPO-15EO composite). The releasing behaviors of gentamicin sulfate from the hemostats appeared to be steady state, (**Fig.1**). In vellanueva bone stain, the hemostats were showed osteoid generation and no foreign body reaction (4 week later). The hemostat containing sHAp and EPO ((sHAp/EPO = 0.20) was found to be effective for the steady state releasing of gentamicin sulfate, biocompatibility, and the inhibition of bleeding effect.

Keywords: hemostatic agent, Thermoplastic resin, phosphoryl oligosaccharides of calcium, Hydroxyapatite Drug sustained release properties, Vellanueva bone stain.

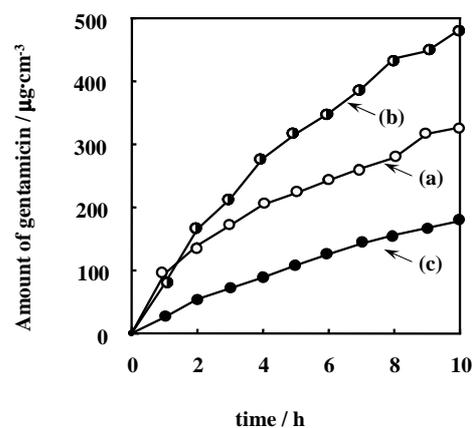


Fig. 1 Changes in amount of gentamicin in PBS(-) solution with increasing time

(a) pure 25EPO-15EO

(b) POs-Ca/25EPO-15EO composite with mass ratios of 0.2

(c) sHAp/25EPO-15EO composite with mass ratio of 0.2 with increasing amount of water.

Scanning electron microscopic study of glass container degradation in infusion solution

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The safety issues of medical products are more and more in the focus of public interest. The medicines in various forms have to fulfil a lot of regulations before they can enter the market and their application is authorised. There are a lot of validated analytical techniques that control the quality, quantity and the stability of the active substances, but the interactions between the medicines and their containers can also result in safety issues.

An infusion applied as supplementary treatment in case of certain cancer types was examined to control the solid particles in the solution. The infusion before bottling is filtered through a sterile filter-membrane that excludes the presence of solid particles in the initial state.

The sample was vigorously shaken and the whole amount was 3 times filtered – on the same disk – through a 0.45 µm PTFE membrane filter. The filter disk was then removed and dried at 50°C for 24 hours. After 2 hours of cooling, the filtered particles were analysed by a Hitachi T1000 scanning electron microscope. An X-ray fluorescent scanning was performed on the particle surfaces to determine the typical elemental compositions. Five types of particles were found:

Fe-Al sedimentation

Al “fibres”

amorphous alkaline type glass particles with high Cl content

CaOy(OH)_y particles with K-Si-Al or K-Al-Si-Na compound crystals

amorphous alkaline type glass particle with high Cl and S content

Particulate contamination was determined from the received sample prior to the SEM analysis. During the particulate contamination determination the sample bottle was opened, and then the vial was recapped with aluminium flip-off cap. This is the origin of the - very rare - Al and Fe particles.

The main fraction - approximately 90% of the whole mass - consist of amorphous alkalyne glass shred. The appearance of S on the particles is explained by the surface treatment of the glass, prior to filling with the infusion solution. The high Cl content on the particle surface is originated from the infusion. The Ca-containing particles show the decomposition of the glass as well. They are solid bubbles, leftover particles in the glass matrix, remained undissolved during the glass manufacturing process.

Sintering and structure formation of ceramics based on plasma-sprayed and chemically precipitated powders

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The phase composition, structure and mechanical properties of ceramic materials based on plasma-sprayed and chemically precipitated ZrO₂ powders were studied. Plasma-sprayed ZrO₂ was characterized by spherical particles and their agglomerates. An average particle size was 0.8 μm. Chemically precipitated powder contained bulk polycrystalline particles with an average size 12 μm. Mixtures with different plasma-sprayed powder content were prepared. Homologous temperature varied from 0.57 to 0.65.

It was shown that the dependence of the porosity and an average pore size from the sintering temperature is nonlinear. Porosity in all materials decreases in the temperature range [0.57 - 0.6]. Further decreasing of porosity volume with the increasing of sintering temperature up to 0.65 is observed in the materials based on mixtures with plasma-sprayed powder content less than 60 vol. %. Porosity in the ceramics contained 80 and 100 vol. % of plasma-sprayed ZrO₂ remains almost the same. The increasing of plasma-sprayed powder content resulted in the decreasing of interconnecting pores quantity and increasing of isolated pores content.

The strength of these materials increased with the plasma-sprayed powder content increasing.

Surface structure and corrosion properties of calcium-phosphate glasses and vitrocereamics in simulated body fluids

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Resorbable glass and glass ceramic scaffolds with controlled biodegradability are attractive candidates for tissue engineering applications [1]. The released ions and the self-assembling layer depend on sample surface properties [2, 3].

We investigated various compositions of CaO-P₂O₅-Na₂O and CaO-P₂O₅-K₂O glasses in order to estimate glass formation, glass stability and activation energy of crystallization as well as dissolution properties of samples. Corrosion behavior in distilled water and simulated biological fluids evidenced an increased dissolution rate with the extent of substitution of P₂O₅ by CaO in samples.

The dissolution of glass and glass ceramic samples in simulated biological media, in static regime, indicates that their corrosion depends on the pH of the solutions, glass composition and local structure. In the first 24 hours one observes two leaching stages relative to the incipient dissolution. In the first stage, the lowest release rate is obtained from the potassium-phosphate matrix in decationized water, while for the whole time the lowest leaching rate is recorded from the sample containing small amount of lime, with CaO/P₂O₅ ratio of 0.06. When the substitution of P₂O₅ by CaO exceeds 50%, the release behavior changes in the investigated media.

Biodegradability and bioactivity of silver containing calcium-phosphate glasses tested in simulated body fluid (SBF) shows that in the first stage of soaking the cations release dominates and at the interface glass – SBF appear proper conditions for a self-assembled bioactive layer. In the next stage the layer developed restricts the cations release through the self-assembled layer. According to calcium and silver ions concentration determined in SBF after different soaking times the growth of the bioactive layer on the surface of investigated samples impresses after four days.

Keywords: *calcium-phosphate glasses; surface properties; corrosion.*

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Sustained Drug Releasing via Porous Channel from Hollow Hydroxyapatite

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Hydroxyapatite (HA) is the most commonly used synthetic bone-graft material due to the main component of bones and teeth. However, many research about combining the biological factors and drugs with HA have been performed since a few years ago. We investigated drug(dexamethasone) release behavior after loading to porous spherical HA granules according to the amount of water and sodium chloride as well as the structure of porous HA.

Nano-sized HA powder was used to form the porous granules. Polyvinyl alcohol (PVA) and carboxy methyl cellulose sodium salt (CMC) were used as a binder and ammonium polyacrylate (AP) was used as a dispersant for the HA slurry. The water content was increased for diversifying the porosity of granules, and the sodium chloride (NaCl) content was increased for changing the pore structure of the granules. The slurry was stirred overnight at room temperature, and then the slurry was dropped into liquid nitrogen where spherical-shaped granules instantaneously formed.

The spheres had unique structures that pore channels continued from center of the sphere to outside like a radial shape. And the pore channels were getting larger with increasing water content. However, the pore channels were irregular with increasing the content of NaCl. Pore volume increased with increasing water content of HA slurry and decreased with increasing NaCl content of that.

We performed the drug release behavior test with water group and NaCl group. Both of the groups had similar pore volume. The HA spheres of the water group and NaCl group were similar in loaded drug content to each other. However, as a result, the drug release behaviors of the water group and NaCl group were presented different pattern. The drug release rate of the NaCl group was slower than that of the water group as we expected. We thought that the irregular pore channel structure of the NaCl group affected delay of the drug release.

For drug release test, dexamethasone (Dex) was loaded as model drug on the prepared HAp granules by immersion method, and the drug release behavior was curved by UV/vis spectrophotometer. As a result, different drug release behavior was observed according to micro-channel structural differences. Therefore, we concluded that Porous spherical HAp granules should be applied to bone grafts as bone filler. These HAp granules have the advantage of having strength comparable to other bone grafts and will be able to function as a drug carrier due to their nano- and micro-interconnected pores as well as micro-channel.

The porous HA spheres should be applied to bone tissue engineering as bone filler. These spherical granules had the advantage of having the unbreakable surface comparing with scaffold (tips of the scaffold are weak point, even if a strong scaffold). And these porous HA spheres will be able to apply as drug carrier due to their micro-interconnective pores.

Studies of Thin Hydroxyapatite Coatings at the Porous Alumozirconium Ceramics

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At present “NEVZ-N” Ltd. implements a set of projects on development of high-technology production of medical items based on nanostructured composite ceramics. The present paper is focused on studies of hydroxyapatite coatings at ceramics. Hydroxyapatite (HA) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is the most prospecting material for bioactive coatings. HA coating at the surface of the medical implants stimulates formation and growth of bone tissue on the implant’s surface; contributes to fast union with the bone and formation of the proper bone tissue; accelerates the process of post-operative recovery. The studies undertaken in our country and abroad show that the method of HF magnetron sputtering is the most optimal method for producing thin (0, 1- 1 mcm) bioactive HA coatings with controlled stoichiometry and structure. To form the coating mechanically synthesized hydroxyapatite (the technology of Institute of Chemistry of Solid State and Mechanochemistry, SD RAS) was used a source of hydroxyapatite. The coatings were studied with use of AFM, IR-spectroscopy, X-ray fluorescence analyses, skretch-tests, in vitro and in vivo. The tests were conducted in the NSTU, Research Institute of Hygieology, TPU.

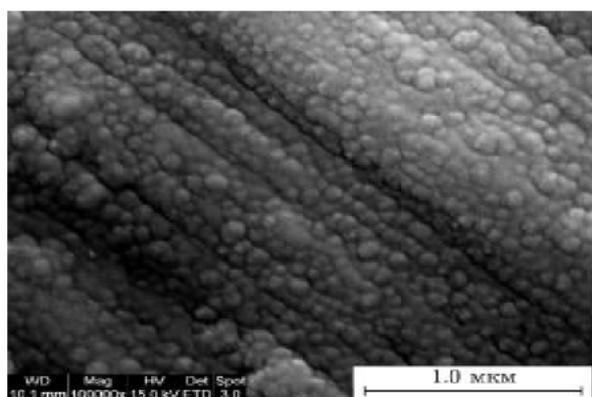


Figure 1

Scanning electronic microscopy of the porous alumozirconium ceramics with HA

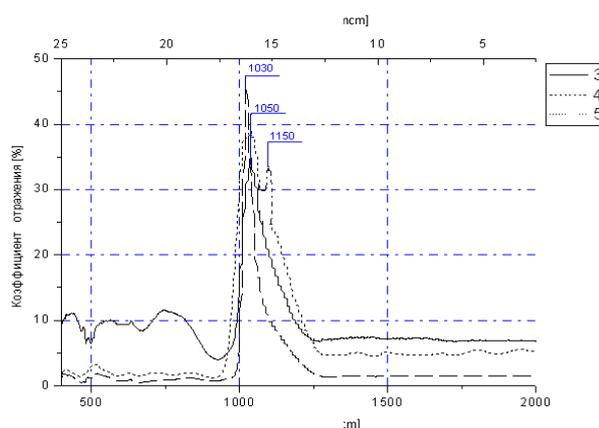


Figure 2

IR spectra of the HA coating at the surface of porous alumozirconium ceramics with various percentage of porosity

The reflection factors of thin HA coatings at the substrates of “dense” (7-9 % porosity) and porous (>30% porosity) ceramics were estimated. During sputtering hydroxyapatite structure was formed at the porous ceramics, while calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ at dense ceramics. Probably, formation of hydroxyapatite coating at the porous ceramics occurred due to adsorbed water in pores at ceramic surface, that reacts with the sputtered substance, this results in HA formation. The results of studies of HA with AFM methods showed that the formed coating has uniform structure within 1 mcm and can be considered as film. According to results of studies a thin uniform HA coatings with controlled thickness, stoichiometry, and structure can be formed at the surface of the porous ceramics with use of the method of HF magnetron sputtering.

The influence of CeO₂ addition on the physical, mechanical and biological properties of alumina/zirconia ceramics

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Zirconia toughened alumina (ZTA) is a high-performance ceramic biocomposite material that combines the excellent material properties of alumina ceramics in terms of chemical stability, hydrothermal stability, biocompatibility and extremely low wear, and of zirconia ceramics that confer superior mechanical strength and fracture toughness. The addition of stabilizing materials such as titanium/cerium oxide can control the phase transformation of zirconia, thereby improving the mechanical properties of the material [1]. The new composites are expected to show a good balance between toughness and strength, as well as a good biological response.

The aim of our study is to investigate the structural, mechanical and biological properties of novel Al₂O₃/3Y-TZP composites prepared by spark plasma sintering (SPS) and their modification upon ceria addition (5 wt% CeO₂). The sintering parameters comprise temperatures between 1330°C -1465°C for 300 s under a pressure of 40 MPa. Scanning electron microscopy, X-ray diffraction and infrared spectroscopic results are reported for structural characteristics. The samples were subjected to mechanical tests like modulus of elasticity, flexural strength, hardness and fracture toughness. Densities of the composites were determined by the Archimedes' method and Vickers hardness was measured under loads of 9.8 N. Properties such as fracture toughness, strength, hardness and elastic modulus themselves are not independent variables that describe a material system. Instead, they are consequences of the material and are affected by variables such as composition, binding strength and microstructure [2]. All these properties showed a correlation with ceria content.

The biocompatibility of the samples with and without ceria is evaluated using an animal model. The specimens implanted in the critical size defect created in femoral bone are analyzed at a specific period (3, 9 weeks) by scanning electron microscopy and EDAX spectrum. Calcium/phosphate ratio is discussed as an indicative of the surface implant coverage for a successful osseointegration. The sections of implanted bone area were subjected to semi-quantitative histological evaluation. No signs of inflammatory reactions, such as necrosis or reddening suggesting implant rejection were found upon histological examination.

Keywords: *alumina-zirconia, ceria, structure, mechanical properties, biocompatibility.*

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Session 2.

Advanced Materials for Extreme Applications

Advanced Materials for Automotive Application

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Sheet metal forming is one of the most important key technologies in manufacturing industry. It may be reasoned by several facts, among them the economy of the sheet forming processes concerning the material and energy consumption, as well as the overall cost efficiency. The automotive industry is one of the main application field of forming processes, thus it is obvious that most of the developments in metal forming are inspired by the developments in the automotive sector.

The main developments in car manufacturing are determined by the continuously increasing requirements arising from the global competition. Among these ever increasing requirements there are many different demands partly driven by the customers' needs and partly by legal requirements, for example: the individualization trends in society is reflected by more and more individualized cars, which also reveals in extreme differentiation in form and function and an explosion of product diversity. What this means in the context of automobile construction is a constant expansion of the product range by means of new model series.

Furthermore, from the customers' side there are further increasing demands on more economical and also more environmental friendly operation supported by legislative means, as well. These require developments to further reduce fuel consumption and at the same time lower harmful CO₂ emission. It is also important to produce more individualized new automobiles with more comfort and optimum safety. The increasing demand on more comfort and optimum safety require even more special services in car operation.

These increasing requirements stated against the automobile industry – besides the construction and design principles – mean the highest challenges on material developments. Many of the before mentioned requirements need the application of light weight constructions which may be met by significant new material developments and new application concepts. Therefore, the application of advanced materials in the automotive industry is of utmost importance. The continuous demand for lightweight automobile constructions led to the elaboration of new materials with higher strength or lower density: the result is the increasing application of various grades of extra- and ultra-high strength steels, aluminum and other lightweight metallic materials, and furthermore the increasing utilization of polymers, ceramic materials and metallic foams, too.

Competitive new developments require the co-operation of scientists of various fields besides materials sciences and manufacturing technologies including natural sciences particularly mathematics, physics and mechanics with an increasing importance of new disciplines of information sciences and artificial intelligence.

Keywords: *advanced materials, automotive industry, metal forming*

Ceramics Reinforced Hetero-Modulus Light Metal Composites with Extreme Hardness and Wear Resistances

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On the basis of several years experiments in development of high performance technical ceramics [1, 2,] and in investigation of hetero-modulus materials and ceramic matrix composites [3, 4, 5] the authors successfully developed a new family of ceramics reinforced hetero-modulus light metal composites with extreme surface hardness and wear resistances. For these hard and wear resistant light metal composite were developed low density, high porosity matrix materials from different sort of sintered ceramics with excellent mechanical strength and hardness. The pore and material structure of ceramic matrix anchored an excellent wetting for a wide range of light metal alloys, so the authors could develop several types of ceramics reinforced hetero-modulus light metal composites with extreme hardness and wear resistances of different density.

Analytical methods applied in this research for tests of material structures were scanning electron microscopy, X-ray diffractions and energy dispersive spectrometry and the hardness and wear resistances were studied by an optical digital scratch tester. Digital image analysis was applied to microscopy results to enhance the results of transformations.

Keywords: *alumina, collision, composite, diamond, dynamic, hetero-modulus, silicon-nitride, strength.*

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Damage and Wear Resistance of Al₂O₃-CNT composites Fabricated by Spark Plasma Sintering

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Carbon nanotubes (CNTs) have attracted great interest because of their unique structural, electronic, physical and thermal properties, such as high electrical conductivity, thermal conductivity and elastic modulus. Therefore, CNTs have been widely studied to use additives or reinforcing materials for advanced or nano ceramic composites for wear resistance application. In this study, we prepared Al₂O₃- CNTs composites with different contents of CNTs with 1~20wt% into the Al₂O₃ ceramics for purpose of improving damage and wear resistance. Al₂O₃- CNTs composites were obtained by SPS (Spark plasma sintering) in condition of 1400~1600°C in vacuum and 30~80 MPa. Hardness and Toughness are evaluated by Vickers indentation. Hertzian indentations using spherical indenter are used for evaluation damage resistance of the composites. The load-displacement curves by spherical indentation are plotted and analyzed. The produced damages on the surface are examined by optical microscope in Nomarski illumination. The wear rate and friction coefficients of the composites are evaluated by ball-on-disk method. Tungsten carbide (WC) ball with a radius of $r = 3.18\text{mm}$ are used for damage and wear test under constant contact load. The results indicate that the damage and wear resistance of the Al₂O₃ ceramics can be enhanced by addition of CNTs in optimum condition.

Keywords: *alumina, CNTs, composites, indentation, wear resistance.*

Direct Synthesis of Large Scale AlN Sheet

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AlN is a functional ceramic with high thermal conductivity (319WmK^{-1}), a high coefficient of thermal expansion ($4 \times 10^{-6}\text{C}^{-1}$), similar to that of silicon, and high electrical insulation ($9 \times 10^{13}\Omega\text{cm}$). These properties are exploited in the heat sink systems of semiconductor chips, in the manufacture of semiconductor components and in functional materials. However, these properties of functional materials could be realized in sintered AlN bulk and sheet. Then AlN powder was formed into bulk and sheet types and then sintered in inert atmosphere at high temperature. Unfortunately, there is little information regarding the direct synthesis method of large scale AlN sheet. In this paper, large scale sheet of AlN was synthesized by the direct nitridation method with an Al-NH₃-N₂-H₂ system. The starting material was Al sheet with 16 micron thickness. Al sheet was transformed in a tube furnace in NH₃-N₂-H₂ atmosphere at 900-1300°C. We could synthesize a large scale AlN sheet with highly crystalline at low temperature. The size of the AlN sheet is 30×100×0.0016mm with only AlN crystal phase. In microstructure analysis, there are fine AlN particles in an AlN sheet and niddle-like AlN particles on the surface. AlN particles decreased from 250 to 100 nm with decreasing reaction temperature in the tube furnace. Large scale AlN sheet synthesized at high reaction temperatures have low oxygen contents.

Keywords: AlN, Synthesis, Al foil, Sheet, Oxygen contents

Effect of Mineral Raw Material Addition on the Properties of Cordierite Based Ceramics

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Cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) is a magnesium aluminium silicate possessing an extremely low thermal expansion [1], low thermal conductivity, high thermal, chemical and mechanical durability, and electric properties close to that of corundum [2]. Because of these properties cordierite-based ceramics have found their use in high-temperature applications like catalytic converter substrates for exhaust gas control of automobiles, refractory material for furnaces or molten metal crucibles, packing material for electronic packing etc [1]. In spite of numerous attempts and extensive research, cordierite ceramics are still under study due to their low linear thermal expansion and provisional attempts to improve preparation processes by using cheaper precursors. Since natural cordierite is very rare, cordierite-rich ceramics must be synthesized by synthetic means. Cordierite based ceramics are difficult to sinter without any sintering aids because the sintering must be accomplished by a liquid-phase process.

The main purpose of the present study is to produce cordierite ceramics using different (traditional ceramic or pressureless and spark plasma sintering) obtaining processes and mineral raw materials of Latvia (dolomites and clays) as the cheap additives. Starting mixtures were composed of synthetic reagents (MgO and $\text{Al}(\text{OH})_3$) with the addition of different dolomites, clay and quartz sand. Powder mixtures were sintered at different temperatures both using pressureless and spark plasma sintering methods. It was stated that secondary crystalline phases like anorthite, spinel, corundum are often present together with a glassy phase and final mixtures determine the properties of the obtained ceramics. Suitable densification levels of investigated compositions were attained using different obtaining methods. Mineralogical composition, microstructure and physical properties were detected using XRD, SEM, water immersion and mechanical strength tests. It was stated that properties of cordierite based ceramics are greatly dependent both on the nature of starting materials and sintering method.

Keywords: *mineral raw materials, sintering, cordierite based ceramics, mechanical strength*

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Effect of several process-control agents on the high-energy ball milling of ZrB₂

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Zirconium diboride (ZrB₂) is one of the most popular members of the short list of ultra-high-temperature ceramics for applications at extreme temperatures in hostile environments. The first detailed studies on ZrB₂ were conducted in the 1960s, and the need for thermal protection shields in future hypersonic flight vehicles has led to a surge of intense research, much of which focused towards mitigating its poor sinterability, which is doubtless one of the greatest obstacles to the development and implementation of ZrB₂ ultra-high-temperature ceramics in aerospace engineering [1,2]. One of the current approaches to promote solid-state pressureless sinterability of ZrB₂ is to refine the starting ZrB₂ powders by high-energy ball milling techniques [1-4].

In a former research work, the high-energy ball milling of pure ZrB₂ powders was seen to produce submicrometre agglomerates of many cold-welded nano-particles, rather than disperse nano-particles [5]. This cold-welding phenomenon could be combated by adding a process-control agent during ball milling of the ZrB₂ powders. Indeed, this strategy has already been applied successfully in the case of graphite [6]. As a further step, the present work reports on the high-energy ball milling behaviour of ZrB₂ in the presence of some other typical process-control agents borrowed from the metallurgy field.

Keywords: ZrB₂, high-energy ball milling, crystallite size refinement.

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First-principles Modeling of Defects Behavior of Ceramic Fuels Under Irradiation

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Uranium dioxide is a most important fuel material used in nuclear reactor, its performance quite relates to the defects behavior under irradiation which arises the deviation from stoichiometric compounds. To investigate the formation, stability mechanism and relevant physical properties of the nonstoichiometric uranium dioxide, comprehensive first-principles calculations have been performed using PAW-LSDA+U method for various complex defects clusters of oxygen atoms in UO₂. Calculations revealed that the stability of the cuboctahedron embedded into the crystal UO₂, clarified the ambiguousness remaining for long in structure of nonstoichiometric UO_{2+x}.

By incorporating the temperature effect, a pseudo phase diagram of temperature and the oxygen concentration has been constructed, and a new physical model of thermodynamic competition between cuboctahedron and point oxygen interstitials is proposed. The interplay of one main fission products, Xe, and the defect clusters in ceramics fuels has been also investigated.

Keywords: *first - principles modeling, nuclear fuel, Uranium dioxide, defects, irradiation*

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High-speed wear testing of selected ceramics in abrasive slurry

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Fast development of process environments has constantly been increasing the level of requirements for materials used in those conditions. Due to increased production speeds, the conditions in sliding contact applications have changed significantly. Therefore it is important to revise the current understanding of wear mechanisms in modern process environments.

A wear testing device has been manufactured for the purpose of cost-efficient simulation of water-containing high-speed sliding conditions. In this wear test a set of samples is pressed against a rolling drum with an adjustable amount of force. Sliding speeds up to 40 meters per second can be achieved while abrasive-containing slurry is fed into the contact interface of the samples and the drum. The slurry used in the tests mainly consisted of water and kaolin, but in some tests coarse alumina ($\text{Al}_2\text{O}_3 + 3\text{TiO}_2$) powder was used for increasing wear rates of the wear resistant ceramics. High-speed wear tests were run with three ceramic materials: silicon nitride (Si_3N_4), silicon carbide (SiC) and zirconia (ZrO_2).

Initial results indicate that at micro-abrasion wear range the increase in sliding speed reduced wear, whereas in severe wear conditions increasing speed accelerates wear. A possible transition from mild to severe wear was observed when changing testing parameters with alumina-containing slurry. The most important material property for the tested ceramics to last in the test environment was sufficient hardness. For the materials that met these hardness requirements, wear rates were dictated by the mutual order fracture toughness. Visual inspection of the worn sample surfaces offers for further discussion about possible wear mechanisms.

Keywords: *wear, ceramic, high-speed, sliding, tribology, testing, aqueous*

High performance concrete pavement on bridges

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In recent years, rapid development can be observed in two areas of life-cycle design of civil engineering structures. One direction is the service life design, which focuses mainly on durability issues and related design approaches to extend the design working life of structures. The other direction is the life-cycle cost analysis that evaluates the cost effectiveness of structures and finds design strategies, by which the life-cycle cost of a structure can be minimized. Majority of structures, to which the application of life-cycle design is desirable, are parts of the traffic infrastructure. These structures are required to work on acceptable technical level for a relatively long service life and need relatively high costs during this period. In the past decades, significant effort was given to provide life-cycle cost basis behind the design of roadways. However, small attention was paid to include bridges into these analyses as well as to carry out life-cycle cost analysis for bridges in itself. This paper focuses on the applicability of high performance concrete (HPC) to roadway bridge decks in order to improve their cost effectiveness and environmental compatibility. HPC is considered as concrete that provides higher resistance against certain effects than traditional concrete (i.e. normal performance concrete, NPC). The relatively higher performance is the consequence of the improvements made by technological measures in one or more of the concrete properties such as workability and compactibility, initial or long-term strength, permeability, proneness to early-age cracking due to hydration heat, shrinkage etc. In majority of cases the primary motivation behind high performance is the improvement of durability of the structure. The research suggests that the maintenance cost of a bridge depends first of all on the durability of the pavement system. Consequently, the life-cycle cost-effectiveness of bridges is based mainly on the proper combination of the load carrying deck and the pavement system. Three existing concrete decks of different cross-section in combination with three alternative pavement systems were structurally analyzed and then compared by an approximate life-cycle cost analysis. The structural design was based on the strict consideration of durability requirements related to different pavement systems. It was concluded that for 100 years of design working life as usual for bridges the integrated concrete deck-pavement superstructure has a clear economic advantage against the widely used, structurally separated deck-pavement solutions.

Influence of metakaolin on chemical resistance of concrete

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Nowadays the most suitable and widely used construction material is concrete. We could develop for every claim in connection with the composition of fresh concrete and the quality of firmed concrete, too. The demand is rise for using special concretes, like high performance and ultra high performance concretes (HPC, UHPC). These are usable in extreme natural circumstances or in very corrosive surroundings (for example: sewage farm, sewer, cooling tower, biogas factories).

The pH value of the commercial sewage is between 7-8, but often this value is around 4 or less. The concrete pipes, which transport the sewage, are under corrosion, because above the liquid level occurs sulphuric acid due to microbes. In this acidic surround could be follow the corrosion of the concrete. When the pH is reduce, the influence of the alkaline acids increase.

The most significant influence has the sulphuric acid. The pH value of this acid is about 1, or less. Earlier in the cooling towers of coal thermal power stations used special coating on the concrete wall. Recently application of high performance concrete without polymeric coating is more general.

Cementitious supplementary materials are widely used to protect the concrete from these corrosive surroundings. Usually used cementitious supplementary materials are ground granulated blastfurnace slag (GGBS), flying ash (FA) or silica fume (SF). In the last years there has been a growing interest in the application of metakaolin. Metakaolin is made by heat treatment, calcination of a natural clay mineral, kaolinit.

In my present research the chemical resistance of mortars in different corrosive surrounds (pH=1 sulphuric acid and pH=3 acetic acid) and the chloride ion migration were studied on series of mortar samples using HTC-test (rapid chloride migration test). To understand the mechanism of the hydration process of metakaolin and cement mixture was also studied using three types of metakaolin. The samples were made with cements with metakaolin replacement (17 %) or without metakaolin. The following cements were used: CEM I 42.5 N; CEM II/A-S 42.5 N, CEM I 42.5 N-S.

We concluded, that the replacement of cement by metakaolin results in significant increases in compressive and tensile strengths and it is preventing the infiltration of harmful substances.

Keywords: *metakaolin, concrete, extreme circumstances, cement hydration,*

Multilayered nanocrystalline CrN/TiAlN/MoS₂ tribological thin film coatings: processing and characterization

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In the present research experiments self-lubricated thin film coatings with nano-layered CrN, TiAlN and MoS₂ were prepared by reactive co-sputtering processes. The multilayer system was deposited by one-fold oscillating movement of the substrates in front of the Ti/Al 50/50%, pure chromium and MoS₂ targets, used as sputter sources of the independently operated DC excited unbalanced magnetrons. The experimental setup and process conditions developed for deposition of tribological thin film coatings are presented in the paper as well. The reactive sputtering process was performed in controlled mixture of Ar-N₂ atmosphere. Coatings were performed for deposition on surface of the hardened HSS steel substrate used for tribological investigation and on surface of thin oxide covered Si(100) substrates used for microstructure investigation by XTEM methodology. The resulting multilayer coatings presented high tribological performance and mechanical characteristics. Due to the embedded MoS₂ inter-layers a low friction coefficient was achieved, value of 0.02 obtained by pin-on-disk experiments. The layers of TiAlCrN assure thermal stability even for high temperatures up to 800-900 °C. This performance can be tuned up even more by introducing Si component in the deposition process and so obtaining multielemental TiAlCrSiN composite layers.

Keywords: *CrN/TiAlN/MoS₂ multilayers, solid self-lubricant MoS₂, nano-structure, nano-scaled coatings, XTEM.*

Multilayer Magnetic Circuit for Millimeter Scale MEMS Air Turbine Generator

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This paper concerns to multilayer magnetic circuits for millimeter scale MEMS air turbine generators. Conventionally, the MEMS micro power generator has been researched on the electrostatic type because of its simple planar structure. However, the output impedance of this type is high. Therefore, the electromagnetic type generator is more desirable. We have proposed that the multilayer magnetic circuits are used for the magnetic part of MEMS micro generator to substitute the complex winding structure. We fabricated various shape of magnetic circuits made by the multilayer ceramic technology which realized the monolithic structure. And then combining the MEMS air turbine, the electromagnetic type power generator was obtained. In additional, a simple winding wire type was compared. The apparent size of the MEMS air turbine part was 3 [mm] cubic. The diameter of the rotor was 1.6 [mm]. Every component of the air turbine was formed by the photolithographic process. The magnetic circuit was based on the green sheet process and combing the machining process. The magnetic material used was nickel copper zinc ferrite that showed low temperature sintering property. And the internal conductor was silver. Although the turn number of the winding wire was more than that of monolithic type, more output power density was extracted from the monolithic structure type. In the monolithic structure, the gap between the magnet and the magnetic circuit was sensitive on output power. Also, the magnetic surrounding structure was effective to suppress the magnetic flux leakage. It is shown that the combination of the MEMS technology and the multilayer magnetic ceramic technology is effective to obtain miniaturized monolithic power generator with high output power.

Keywords: *Multilayer ceramic, Ferrite, MEMS, Generator, Air turbine,*

Oxide Thermoelectric Materials Promising for Heat-to-Electricity Direct Conversion from Mid-to-High Temperature Waste Heat

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Thermoelectric power generation directly converts heat energy to electricity via the Seebeck effect in semiconductor solid materials over which a temperature gradient exists. The conversion efficiency of the thermoelectric power generation is evaluated by the dimensionless figure-of-merit, $ZT = S^2\sigma T/k$, where S is the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity of the materials, and T is the average operating temperature in K. The criterion generally accepted for thermoelectric materials to be practically competitive is $ZT \geq 1$. The thermal conductivity of solids mainly consists of the electron and phonon contributions as $k = k_{el} + k_{ph}$. Since the Wiedemann-Franz law, $k_{el} = L\sigma T$, where L is the Lorenz number, tells us that the contribution of carrier electrons is proportional to σ , no one will be benefited by reducing k_{el} , and a significant reduction of k_{ph} with keeping σ intact is desired for higher ZT . Selective scattering of phonons without affecting transport of conduction electrons is therefore an ultimate target for thermoelectric material research. Candidate materials are hence required to overcome a difficult trade-off between heat and charge transport. In order to exploit mid-to-high temperature waste heat, excellent stability of oxide materials at high temperature in aerobic conditions is definitely prospective. Rapid progress in the thermoelectric performance of oxide ceramic materials has been conducted virtually exclusively by Japanese researchers, resulting in more than 10 times increase in their ZT values within the last two decades. This has caused a revolutionary change in the direction of thermoelectric materials research, in which oxide materials had been disregarded as a potential candidate until early 1990s. Promising oxide thermoelectric materials having been discovered include CaMnO₃-based perovskites, Al-doped ZnO, layered cobalt oxides represented by Na_xCo₂O₄ and Ca₃Co₄O₉, and SrTiO₃-related phases. Nevertheless, low carrier mobilities due to their ionic characters and high lattice thermal conductivities due to their light constituent elements are still inherent disadvantages of the oxide thermoelectric materials. Zinc oxide doped with Al has been one of the best n-type bulk thermoelectric oxides since our report in 1996. In this paper, our recent results for reducing the high thermal conductivity of the ZnO-based oxide will be discussed in terms of importance of nanostructure in the oxide. A bulk nanocomposite structure is found to be important to achieve a considerable reduction in the thermal conductivity with keeping high electrical conductivity, leading to a remarkable improvement in the ZT value of the ZnO-based oxide.

Phase content and structure of PSP-zirconia powders after annealing

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This work is devoted to studying of phase content and crystalline structure of annealed zirconia based powders. Powders were obtained by plasma-chemical method and contained 3-20 wt.% of MgO were annealed at temperatures 700-1400°C during one hour. Analysis of phase content and crystalline structure was carried out by X-ray method.

In initial powders were presented of monoclinic (*m*-ZrO₂), tetragonal (*t*-ZrO₂) and cubic (*c*-ZrO₂) zirconia, increasing of magnesia concentration from 3 up to 20 wt.% leads to growth of *c*-ZrO₂ content from 80 up to 90%. In powders doped with 15 wt.% of MgO was found magnesia phase. An increasing of magnesia up to 10 wt. % were observed a decreasing of lattice parameter of *c*-ZrO₂, and its doesn't changes with next increasing of MgO content. This may be connected with solubility limit of MgO. Lattice parameter of *m*-ZrO₂ doesn't changes at all magnesia contents.

There were no changes of phase content at 700°C. In the 3 and 5 wt.% MgO annealed at 900°C the decomposition of cubic ZrO₂ into *m*-ZrO₂ and MgO was found, concentration of *m*-ZrO₂ was about 90%, for 10 - 20 wt.% MgO powders decomposed into tetragonal zirconia and MgO. After annealing at 1400°C the phase content of all powders was presented by *m*-ZrO₂ and MgO. At annealing temperature 700-1400°C were observed an increasing of CDD (coherent diffraction domain) size of *m*-ZrO₂ from 24 up to 45nm and from 16 up to 32nm for cubic zirconia.

Keywords: *zirconia, magnesia, plasma-chemical, annealing, CDD*

Properties changes of TiC_x after mechanical activation treatment

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Parameters of structure, morphology and specific surface area of titanium carbide powder subjected to mechanical activation processing have been investigated. It was established that non-stoichiometric titanium carbide powder is consist of two phases with different ratio of carbon to titanium TiC_{0.68} and TiC_{0.53}. Mechanical activation of powders leads to a decrease of sizes of the coherent diffraction domains and increase of residual microstresses level of crystal lattice. A bimodal size distribution of particles has been found in the investigated powder, as a result of mechanical treatment there is a reduction the average particle size from 3.2 to 1.5 μm and from 12 μm to 7.3 for the first and second modes respectively. In this case amount of particles smaller than 4 μm increases from 40 to 85%. The fracture of particles TiC_x occurring under influence of mechanical activation with this high level of residual microdistortion of crystal lattice leads to a significant increase in specific surface area from 0.6 m²/g to 3.4 m²/g.

Slipping properties of ceramic tiles /Quantification of slip resistance

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Regarding the research and application of ceramic tiles there is a great importance of knowing precisely the interaction and friction between surfaces. The slipperiness is always interpreted relatively since it depends on the person in motion, type of footwear and dry, wet or oily circumstances. In some workplaces, there is an increased risk of slipping due to work with slippery materials, such as: grease, oil, water, food, food scraps, dust, flour and vegetable waste. For the time being in Hungary there aren't any clear instruction, guide or unified testing method for determining the slip resistance of ceramic tiles. The manufacturers lay emphasis on aesthetics instead of safety in use. Since the publication of harmonized standard EN 14411:2007 "Ceramic tiles - Definitions, classification, characteristics and marking" the number of expertises has increased especially in the issue of slip resistance which is the most controversial feature of ceramic tiling. This property is often incomplete or inaccurate, however causing slip and fall accidents, of which importance are often underestimated, yet accidents are affected greatly by the material, surface structure of floors, and possible contamination. The risk of slipping depends not only on choice and performance of tiles, but also human and environmental factors. It can be stated that the multiple testing of properties resulting from surface patterns, fixing, maintenance and cleaning is essential. It is necessary to examine the structure of materials in order to get adequate correlation. That is why measuring techniques of surface roughness, an important contributor to slip resistance and cleaning, is fundamental in the research. Measuring of slip resistance of pavement is such a complex problem, therefore in the lack of a consistent, clear EU standard; it is practical to use more method in combination. In the testing process different procedures are being applied. By comparing the obtained test results, relationship between individual methods of analysis and values could be determined and based on these information recommendations could be prepared concerning the selection and application of tiles. Keywords: ceramic tile, slip resistance, structure of material, surface roughness.

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Synthesis and Piezoelectric Properties of Ba_{1-x}Li_xTiO_{3-x/2} by a Solvothermal Approach

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Lead-based perovskite solid solutions of Pb(Zr, Ti)O₃ (PZT) have been widely used for piezoelectric devices due to their large piezoelectric constants at a relatively high temperature. Nowadays, because of the toxicity of lead oxide, it is desired to use lead-free piezoelectric materials in place of PZT for environmental protection, therefore, there is an increasing interest of investigating lead-free piezoelectric materials. BaTiO₃ has become one of the most important ferroelectric materials used in the electronics ceramic industry. However, the piezoelectric properties of BaTiO₃ were insufficient compared with PZT. It was reported that the addition of Li₂CO₃ as a sintering additive, could improve both the sinterability and the piezoelectric properties [1]. It was indicated that Li⁺ was doped into the lattice of BaTiO₃ during its sintering. It was found that piezoelectric ceramics made from powders synthesized by solvothermal processes exhibit improved sinterability, poling property and piezoelectric properties, because of their higher homogeneity of chemical composition, fine particle size and/or unique morphologies such as plate- and cubic-shape.

In the present study, Ba_{1-x}Li_xTiO_{3-x/2} ($x = 0, 0.01, 0.02, 0.03, 0.04, 0.06$) particles were synthesized by a solvothermal approach at 200°C. The products consisted of 50-100 nm in diameter, and could be sintered to almost full theoretical density (> 95%) at a low temperature such as 1100°C. The sinterability and piezoelectric property of Li-doped BaTiO₃ were improved by doping with Li ion. The highest piezoelectric constant, d_{33} , (260 pC/N) and electromechanical coupling factor, k_p , (43.7%) could be realized at x value of 0.03. The Curie temperatures of all samples were 130°C, which did not change very much with the amount of Li-doping.

Keywords: BaTiO₃, Piezoelectric materials, Solvothermal approach,

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The effect of thermal processing parameters on the microstructure of extruded and sintered TiO₂ ceramics

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Titanium oxide is one of the most important inorganic products in chemical industry. It is widely used in various fields - in photocatalysis, biomaterials, self-cleaning elements and in electronics. Chemical stability, non-toxicity, ease of availability and relatively low price are significant advantages for its introduction into industry. The electrical properties of nonstoichiometric compounds (TiO_{2-x}) appearing after reduction differ from those of stoichiometric TiO₂.

Extrusion is perspective forming technology for obtaining of objects with certain profile. Nowadays it is widely used ceramic materials forming technology, because it is relatively cheap and productive.

During the investigation extrusion mass preparation technology for obtaining of dense and qualitative samples was developed. Additives used for mass preparation includes water, plasticizer and binding agent.

To obtain high quality samples not only the composition of extrusion mass has to be developed but also the extrusion, debinding, calcination and sintering parameters have to be investigated.

In this work the densities and microstructure of extruded samples (bars) and the influence of these parameters on electrical properties was investigated.

Keywords: *TiO₂, extrusion, density, microstructure, electrical properties*

Acknowledgements

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The impact of work environment on chemical and phase composition changes of magnesia-spinel refractories used as refractory lining in secondary metallurgy device

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This paper presents the results with an evaluation of the chemical corrosion of magnesia-chrome refractories in snorkel of RH degasser for vacuum degassing of steel after 24 RH processes. Silicate slag enriched with iron and manganese is the most corrosive agent for the used MCr refractories. Changes in the chemical and phase composition of the MCr refractories caused by the slag corrosion were determined. For the purpose, both XRF and XRD techniques were applied. From the X-ray diffraction analysis, our results showed that there was no significant changes in the type of phases present. Whereas, the diversification of the chemical composition of non-corroded and corroded magnesia-chrome refractories was found by means of SEM and EDS methods. According to EDS chemical analysis, the changes in the elemental composition took place both in the main components and silicate binding phase where the new formed phases were detected. Magnesia-chrome refractories (MCr) were produced and tested under industrial conditions.

This work is supported by the grant no UDA-POIG.04.04.00-18-010/09-00 of the Polish Government.

The research and development of the oxidation resistant interphases for SiC fiber reinforced ceramic matrix composites

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It is widely accepted that the mechanical behavior of high-temperature ceramic matrix composites reinforced by SiC fibers is highly depend on the interphase between fibers and matrix. The purpose of this work is to develop and to characterize the interfacial coatings for new generation SiC fibers for ceramic matrix composites. As interfacial coatings, the refractory carbides and oxides, including stabilized zirconia, have been investigated. The surface chemistry, morphology, composition, topography, roughness, local mechanical and adhesive properties of interphases were evaluated by different analytical techniques, including SEM/EDS, TEM, XPS, XRD, AFM, micro Raman analysis. Direct adhesion force mapping measurements on as-received and coated fibers were performed by atomic force microscopy. Mechanical properties of the fiber/matrix interface in composites were investigated using an indentation method. The obtained results provide new insights into composite material mechanical performance.

Zirconia-based nanopowders synthesized by ultrasonic-assisted precipitation method for extreme applications

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It has been studied structure and properties of nanocrystalline ZrO_2 - Y_2O_3 powders, synthesized by co-precipitation method with ultrasonic treatment of the solution. It was shown that the powders are nanocrystalline with a typical crystallite size of 10 nm. Annealing leads to the increasing of an average crystallite size up to 50 nm. It was observed that the powder particles are polycrystalline aggregates containing up to 10^6 crystallites. Estimated activation energy for grain growth is equal to 55 - 60 kJ/mol, which indicates that the surface diffusion is dominant mechanism of grain growths. It was shown that the synthesized powders have tetragonal structure, and the degree of tetragonality depends on the size of crystallites, in agreement with literature data and it was shown that the increasing of the degree of tetragonality is observed when the crystallite size is less than 12 nm, at low annealing temperatures, due to non-uniform distribution of yttrium in their synthesis, aligned with the subsequent the annealing of powders. The properties of ceramics after sintering of these powders are studied.

Keywords: powder system ZrO_2 - Y_2O_3 , the co-precipitation method, ultrasonic dispersion.

ZrW₂O₈ in the sintered ceramic composites

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Zirconium tungstate ZrW₂O₈ with an isotropic negative thermal expansion over a wide temperature range from 0.3 to 1050 K is of a great scientific and technological interest. The using of such materials in the technology of composite materials allows to obtain composites with high strength properties due to different values of the thermal expansion coefficient (CTE) of the initial materials. ZrW₂O₇(OH)₂*2H₂O powder obtained by co-precipitation was calcined at 500 °C for 1 h in air. Then the powder was annealed at 1100, 1150, 1200 and 1250 °C. After heating the powders were quenched. It was established that the powder synthesized at 500 and 1100 °C consists of irregular shape agglomerates. Further annealing leads to the appearance of needle-shaped and isolated spherical particles. When temperature increases the length of needle-shaped particles increases from 8.2 to 16.3 mm but its width varies slightly. X-ray diffraction analysis showed there were the zirconium oxide ZrO₂ and tungsten oxide WO₃ phases in the material at low temperature, and the formation ZrW₂O₈ began at temperatures more than 1100 °C. The lattice parameter ZrW₂O₈ was equal to $a = 9,1482 \text{ \AA}$ at 1100 °C that agrees well with the literature. It was shown that the synthesized material has a negative thermal expansion in the temperature range from 580 to 620 °C and it was equal to $-12.1 * 10^{-6} \text{ C}^{-1}$.

The properties of the ZrO₂ - ZrW₂O₈ composites with different contents of the volume fraction ZrW₂O₈ were studied.

Session 3.
Glasses and related materials

Alkali–silica reactivity of expanded glass granules in structure of lightweight concrete

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Lightweight concrete has become popular construction material because of several advantages over conventional concrete. Lightweight concrete performs good compressive strength, durability and the most important advantages – low density and improved thermal conductivity. Main component in the lightweight concrete, which is responsible for previous noted properties, is aggregate. Expanded clay, shale or glass aggregates and natural porous materials like vermiculite or pumice is ordinary used as aggregate in the lightweight concrete mixtures. There are found a lot of investigations regarding to alkali silica reaction (ASR) between cement and expanded glass aggregates in the literature. In contrary expanded glass granules, which is relatively new product in the market of building materials, is not well investigated. Therefore the new types of the lightweight granules made from waste glass and eight types of cement with different chemical and mineralogical composition were examined in this research. Expanded glass granules used in this research is commercially available material produced by Penostek. Lightweight concrete mixtures were prepared by using commercial chemical additives to improve workability of concrete.

The aim of the study is to identify effect of cement composition to the ASR reaction which occurs between expanded glass granules and binder. Properties of expanded glass granules were tested: loose bulk density, water absorption, material density and material porosity were determined. In addition properties of fresh concrete like density, flow table test and cone slump as well as air content were determined. Mechanical and physical properties were determined for all specimens. Tests with scanning electron microscope and microstructural investigations were performed for expanded glass granules and hardened concrete specimens before and after exposing them in alkali solution. The ASR test was processed according to RILEM AAR-2 testing recommendation.

Keywords: *Expanded glass granules, Lightweight concrete*

Controlling glass colour

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Many commercially useful glasses contain ionic species that can exist in more than one oxidation state. The proportions of ions in each state depend on factors such as glass temperature, melting atmosphere and host composition. Where two or more such species exist then mutual redox reactions on cooling the melt also play a major role in defining the final equilibrium. This paper will explore mathematically the consequences of this for glass transmission control, decolorising, and refining and will examine quantitatively systems such as Fe/Cu and Fe/Ce, including a comparison with experimental results. The paper will also include a consideration of colour stability for glasses that undergo different processing steps around the glass transition temperature e.g. thermal toughening. The importance of redox reactions in creating stained glass will also be discussed.

Comparison of Microstructures and Scratch Strength of Thin Film Coatings on Glasses of Mirrors and Automobile Windscreens

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The aesthetic appearances and quality of glass mirrors very strong depend on thickness and microstructures of fixing flux thin film layers and used silver film coatings. Similarly to this in the automobile industry the efficiency of windscreen heating also very strong depends on used materials and on microstructures of fixing thin film coatings and heater filaments as well as on quality of their interfaces between themselves and screen glasses [1]. The material structures and scratch properties of single and multilayer fixing fluxes and silver thin film coatings on windscreens of different European and Asian automobile were studied by the authors and were compared with the silver coatings of glass mirrors. Most of the fixing thin film layers and silver coatings on glasses of automobile windscreens had lot of bubbles and cracks in their microstructures and gaps with different thickness on their interfaces. The realized scratch tests had shown very strong influences of surface roughness [2] and these cracks bubbles [3] and gaps on the values of scratch resistance, acoustic emission and micro-hardness of these coatings

To examine the material structures of the fixing flux thin film layers and silver coatings scanning electron microscopy (SEM) was used by the authors. The adhesive strength, scratch resistance, acoustic emission, nucleation and propagation of cracks were studied by an optical digital mechanical scratch tester.

Keywords: *coating, glass, interface, microstructure, scratch, strength, thin film.*

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Cu-Hf-Al amorphous/nanocrystalline composite particles produced by milling

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$\text{Cu}_{(54-x)}\text{Hf}_{(36+x)}\text{Al}_{10}$ (at%) (x=0; 2; 4) amorphous/nanocrystalline composite particles were prepared by ball-milling. The crystalline master alloy were prepared by induction melting under purified argon atmosphere. Before the mechanical milling the master alloy ingots were grinded to particle size of < 320 μm .

During the mechanical amorphization the grinded ingots were milled for different time and with several interruptions in order to analyse the structure of the powders. The mechanical milling was performed in a Pulverisette2 high energy planetary ball-mill in argon atmosphere using stainless vial and balls with a diameter of about 3 mm, 5 mm and 10 mm. The ball-to-powder ratio was 20:1 [1].

The milled powder was analysed by XRD to define the amorphous fraction, by SEM to realise the microstructure, by DSC to observe the processes during heating in the powder.

Keywords: *amorphous/nanocrystalline powder, ball milling, XRD, SEM*

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Effect of La₂O₃、 Nb₂O₅、 Bi₂O₃ additives on optical and thermal properties of boron silicate glasses

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In recent years, glass molding technology, which takes the place of conventional glass grinding and polishing technology, has been used widely to produce the aspheric lenses. In glass molding, a glass lens is produced by compressing glass preforms at a high temperature around the yield point of glasses and replicating the shapes of the mold cores to the lens surface without need for further machining process. The lifetime of the molds is of critical concern in mass production and depends on the molding temperature. Therefore, the glass with low transition temperature and high refractive index is necessary for glass molding process. In this study, the glass system of SiO₂-B₂O₃-Li₂O (SBL) glasses containing La₂O₃, Nb₂O₅, Bi₂O₃ respectively were synthesized and investigated in terms of refractive index, transmittance spectra in the visible region, glass transition temperature (T_g). The glass does not contain lead, arsenic, fluoride and other harmful compositions. The results show that under the same addition, glasses with La₂O₃ have the lowest refractive index (nd = 1.7400), and the highest glass transition temperature (T_g = 678°C) as well as transmittance (80 ~ 89%). Addition of Bi²O³ will increase refractive index (nd = 1.7702) and decrease glass transition temperature (T_g = 622°C), but transmittance is worst (78 ~ 85%). The variation in different physical parameters such as T_g, refractive index and transmittance with different ratio of La₂O₃, Nb₂O₅, Bi₂O₃ have been analyzed and discussed in terms of change in the glass structure.

Keywords: *optical glass, refractive index, glass transition temperature*

Fabrication of transparent sintered ZnO-B₂O₃-Bi₂O₃ glass body by pressureless firing and hot isostatic pressing

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The optimum conditions for the fabrication of transparent glass body in the ZnO-B₂O₃ (ZB) and ZnO-B₂O₃-Bi₂O₃ (ZBB) systems were examined by the combination of pressureless firing and hot isostatic pressing (HIP). On the basis of the transition temperature (T_g) of ZB glass being 614.7°C, the cylindrical ZB powder compact with a diameter of 15 mm and a thickness of 7 mm was pressurelessly fired at a temperature between 590 and 670°C in air and then hot isostatically pressed at a temperature between 610 and 640°C for 12 h in 80% Ar-20% O₂ atmosphere under the pressure of 150 MPa. The pressurelessly-fired ZB body possessed the maximum relative density of 99.1% at 620°C for 15 min. However, the resulting ZB body contained the pores with diameters of approximately 2 μm, showing the opacity due to the scattering of light at the pore sites. Then the pressurelessly-fired ZB body was further isostatically pressed at 630°C for 12 h under the pressure of 150MPa in order to eliminate the residual pores. The resulting ZB body showed the transparency, and the average transmittance of this glass body attained 62.8% (**Fig. 1(a)**). A further investigation was conducted in order to make clear the minimum pressure needed for the fabrication of transparent ZB body. The transparent ZB body could be obtained at the applied pressure of 80MPa, whereas no transparency appeared at 20 MPa. Thus the pressure needed for the transparency was found to be approximately 80MPa or higher.

In order to obtain the transparent glass body at comparatively lower temperature, the fabrication conditions of ZBB glass were examined, because the T_g of ZBB glass was 480.3°C and lower than the case of ZB glass. The cylindrical ZBB compact was pressurelessly fired at a temperature between 480 and 520°C in the O₂ atmosphere, and hot isostatically pressed at 490°C for 12 h in 80% Ar-20% O₂ atmosphere under the pressure of 150 MPa. The relative density of ZBB glass body pressurelessly-fired at 500°C for 2 h was 98.8%. Due to the hot isostatic pressing at 490°C for 12 h, the transparent ZBB glass body was obtained, and the average transmittance attained 66.3% (**Fig. 1(b)**).

Overall, the transparent ZB and ZBB glass

bodies could be fabricated using the optimized pressureless firing and hot isostatic pressing.

Keywords: Sintering of glass, Transparent glass body, Hot isostatic pressing, Atmosphere control

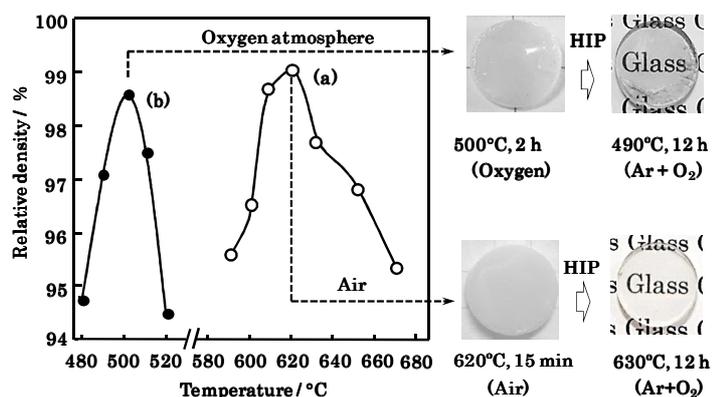


Fig. 1 Relationship between pressureless firing temperature and relative density of (a) ZB glass body and (b) ZBB glass body, together with photographs of their appearance.

Note that the pressureless firing times of ZB and ZBB glass bodies at each temperature were 15 min and 2 h

Investigations on thermal, optical and structural properties of phosphate glasses containing terbium ions

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The present work deals with aluminophosphate glasses belonging to the $\text{Li}_2\text{O}-\text{BaO}-\text{Al}_2\text{O}_3-\text{La}_2\text{O}_3-\text{P}_2\text{O}_5$ system containing Tb^{3+} ions, prepared by a non-conventional wet route [1]. Methods as Induced Coupled Plasma-Mass Spectrometry (ICP-MS), Induced Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and X-Ray Fluorescence (XRF) have been used to establish the elemental composition of these vitreous materials. Differential Scanning Calorimetry and Thermogravimetric Analysis (DSC-TGA) provided information regarding the phase transformations that took place during the heating process and the associated thermal effects. The influence of the Tb^{3+} ions on the optical properties of the phosphate glasses has been investigated in relation with the structural characteristics of the vitreous matrix. The optical behavior has been studied by ultra-violet-visible (UV-Vis) spectroscopy, revealing electronic transitions specific for terbium ions. Tb^{3+} - doped glasses present few optical absorption peaks in the UV and Vis domains used as excitation wavelengths to generate fluorescence emission. Structural information via vibration modes was provided by Fourier Transform Infrared (FTIR) absorption spectra in the $400-4000\text{ cm}^{-1}$ range. Absorption peaks specific for the vitreous phosphate matrix were put in evidence as P-O-P symmetrical and asymmetrical stretching vibration modes, P-O-P bend, PO_2^- symmetrical and asymmetrical stretching vibration modes, P=O stretching vibration mode as well as P-O-H water absorbance. Raman spectra acquired in the $100-4000\text{ cm}^{-1}$ range by 488, 514 and 633 nm laser excitation sources disclosed peaks also specific for the phosphate matrix, proving the role of phosphorous oxide as a vitreous network former. Fluorescence spectroscopy measurements have been performed by excitation in the UV domain (377 nm) which resulted in the most significant fluorescence peaks in the Vis domain (540 and 547 nm). Information about the elemental compositional homogeneity of the Tb doped-glass is revealed by Scanning Electron Microscopy/Energy Dispersive Spectrometry (SEM/EDS).

Keywords: *phosphate glass, rare-earth ions, optical properties, glass structure, fluorescence*

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Light Scattering Glass Material Modified by Surface Ion Exchange for Energy Efficient using in Technical and Decorative Lightening

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The new data related to the new scattering glass material manufacture by the lime silica glass modification with the surface ion exchange paste (SIEP) will be presented in report. There are demonstrated the results of scattered light spectrums, screen illumination by the light passed through a glass and depolarization of glass with the modified surface and with/without the Au nanolayer (10 nm thick). The modification of the glass surface allows improve light scattering characteristics – light energy losses and the light scattering uniformity in comparison with the traditional methods of glass surface treatment – sandblasting and chemical etching (Fig. 1).

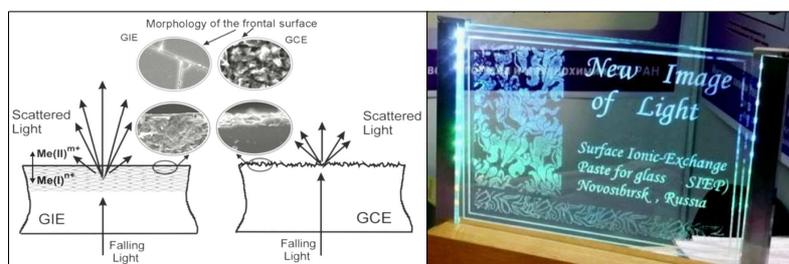


Figure 1. Schematic diagram of light scattering in the glass surface layer of glass samples modified by the surface ion exchange (GIE) and by the surface chemical etching process (GCE).

Figure 2. The glass sample decorated by SIEP and illuminated by coloured LEDs (gold medal ITE Siberian Fair,

The glass samples modified by the surface ion exchange are characterized by the more effective (in tree times) simultaneous light transmission and light scattering taking place in the modified glass surface layer; by the more strongly pronounced spectral dependence of the scattered light and by the stronger angular dependence of the scattered light. The light intensity of the scattered light in the full internal reflection regime is noticeably greater (up to 16 times!) in comparison with the chemical etched glass. In authors' opinion, such optical data may be useful in illuminating engineering for the technical or decorative applications of glasses (Fig. 2). Presented glass scattering material can be used as technical or decorative illuminating glass for manufacture of glass production: luminariers; light screens and indicator panels, displays; decorative or technical images on glass; elements of furniture design; elements of architectural design; glass sculptures and others [1-4].

Keywords: 1 - glass, 2 – optical properties, 3 - ion exchange, 4 – lightening, 5 – decoration

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Lithium disilicate based glasses and glass ceramics in the $\text{Li}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$ system

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This work aims to shed some light on the structure and thermo-physical properties of lithium disilicate glasses in the system $\text{Li}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$. A glass with nominal composition $23\text{Li}_2\text{O}-77\text{SiO}_2$ (mol%) (labelled as $\text{L}_{23}\text{S}_{77}$) and glasses containing Al_2O_3 and K_2O with $\text{SiO}_2/\text{Li}_2\text{O}$ molar ratios (3.13–4.88) were produced by conventional melt-quenching technique in bulk form. The glass-ceramics (GCs) were obtained from nucleation and crystallisation of monolithic bulk glasses and the structure of glasses as investigated by magic angle spinning-nuclear magnetic resonance (MAS-NMR) depict the role of Al_2O_3 as glass network former with fourfold coordination, i.e., Al(IV) species while silicon exists predominantly as a mixture of Q^3 and Q^4 (Si) structural units. The qualitative crystalline phase evolution in glasses was followed by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The possible correlation amongst structural features of glasses, phase composition and thermo-physical properties of GCs has been discussed.

Keywords: *Sintering, Thermo-physical properties, Glass-ceramics, Lithium disilicate*

Point fixing of glass

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Glass is a rigid material and for a long time its brittleness was a well-known property besides its transparency. With the development of glass strengthening methods, glass becomes an often used building material also in load bearing structures [1]. With the increase of transparency, reduce of appearance of supporting structure becomes an important factor, therefore the number of point-fixed glazing increases. Usually cylindrical bore hole is drilled or a cone shaped element is penetrating into the glass pane to carry the loads. The bore hole causes high stress concentrations in glass, therefore heat-strengthened or tempered glass should be used. Stresses in the region of bore hole can dominate the selection of glass thickness.

Glass strength is influenced by many factors during the production or lifetime of glass. There are many affects which can decrease the strength of a glass pane. The strength of the glass product depends e.g. on edge finishing techniques as well as the handling of glass panes during and after the manufacturing process.

Requirements are increasing on the safety of glazing in public buildings e.g. used in balconies, balustrades, staircases, overhead glazing. Therefore, this paper is focused on laboratory testing of single and laminated glasses with bore holes and also demonstrates the influencing factors by creating load bearing glass structures. Surface strain measurements of tension loaded specimens – at the middle of the pane and near the glass hole – were investigated and also large scale tests on point-fixed balustrade glasses were carried out.

Keywords: *glass, point fixing, tempered, bore hole, strain, load bearing*

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Study of Bi₂O₃ nucleated melilite based glasses and glass–ceramics for functional application

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Bi₂O₃–nucleated melilite based glasses and glass-ceramics in the system CaO–MgO–Al₂O₃–SiO₂–La₂O₃ have been appraised for sealing applications in solid oxide fuel cells (SOFCs). The properties and structure features of glasses were investigated by density, dilatometry, infrared spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The crystallization kinetics and the sintering behaviour of the glasses were investigated by differential thermal analysis and hot stage microscopy. All glass compositions exhibited single-stage shrinkage behaviour. X-ray diffraction in conjunction with the Rietveld-RIR technique were employed to quantify the crystalline and amorphous phases in the glass-ceramics sintered under non-isothermal conditions for 1 h within the SOFC operating temperature range (850–900 °C). Merwinite and melilite (the solid solutions of akermanite and gehlenite) were revealed as the major crystalline phases formed in glass-ceramics. The amount of melilite phase significantly increased from 850 to 900 °C at the expenses of merwinite. The amount of merwinite phase increased with increasing Bi₂O₃ contents in glass-ceramics sintered at 850 °C, while it decreased in glass-ceramics sintered at 900 °C. The coefficients of thermal expansion (CTE) (10.2–10.9) × 10^{–6}K^{–1} for the glasses, and (9.81–11.2) × 10^{–6}K^{–1} for the glass-ceramics are in good agreement with those of ceramic electrolyte, 8YSZ and metallic interconnect, Sanergy HT. Well matching CTE values and good adhesion to SOFC components (8YSZ and Sanergy HT) allow proposing some experimental compositions for further experimentation as SOFCs' sealants. Glasses demonstrating bulk nucleation can attract interest for other functional application as optical and electronic devices

Keywords: *glass-ceramic sealants, Solid oxide fuel cells, melilite, chemical interactions*

The Carbon Nanotubes Formation at Room Temperature as a Result of the Detachment of the Gold Nanolayer Fragment from the Glass Substrate

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The results of investigation of boundaries special features formed after the detachment of thin gold layer (50 - 200 nm thick) from soda lime glass substrate are presented. SEM study was carried out by microscope JSM-6460RV (Joel, Japan) with X-ray EDS installation (INCA Energy-350, Oxford Instruments, Great Britain). The Au layer was deposited on the glass surface by Auto Fine Coater JFC-1600 (Jeol, Japan). The detachment of fragments of the Au layer was carried out by vertical loading applied to a metal holder glued to the Au layer.

It was shown that the morphology of detachment boundaries of the thin Au layer depends essentially on the kind of glass substrate surface: the smooth glass surface without pre-treatment, the chemical etched glass surface [1] and the glass surface modified by surface ion exchange [2, 3] (Fig. 1a-c). So, the detachment boundaries of Au layer from the smooth glass substrate without pre-treatment are sharp and even as cracks on glass without surface treatment (Fig. 1a). The Au layer's surface on chemical etched glass is characterized by hills, hollows, steps and kink sites. Accordingly, the observed Au detachment boundaries are uneven, with irregular prominences (Fig. 1b). In the case of the glass substrate modified by surface ion exchange, the detachment boundaries of gold layer coincide exactly with a system of microcracks formed in surface glass layer during surface ion exchange of ions Na⁺ in glass on ions Li⁺ from the surface ion exchange paste (SIEP) (Fig. 1c).

Unexpectedly, it was found that carbon nanotubes are formed after the detachment of thin gold layer fragments from glass substrate and keeping of samples with air contact at room temperature. The formation of nanotubes on thin gold layer is localized near detachment boundaries (Fig. 2 a – c). The results of X-ray EDS measurements have confirmed that observed nanotubes are carbon nanotubes and areas of the carbon observation coincide exactly with area of nanotubes localization (X-ray EDS mapping). In authors' opinion, it was observed the mechanochemical effect of the thin gold layer detachment on catalytic properties of gold film on glass substrate, which leads to Au catalytic activity increasing and carbon nanotubes formation in atmosphere with carbon containing impurities. This assumption has been confirmed by experiment of observation of the carbon nanotubes formation at keeping of samples after the gold layer fragment detachment in ethylene atmosphere (Fig. 3) [4].

Keywords: 1 - thin layer, 2 - carbon nanotubes, 3 - gold, 4 - ion exchange, 5 - glass surface, 6 - adhesion

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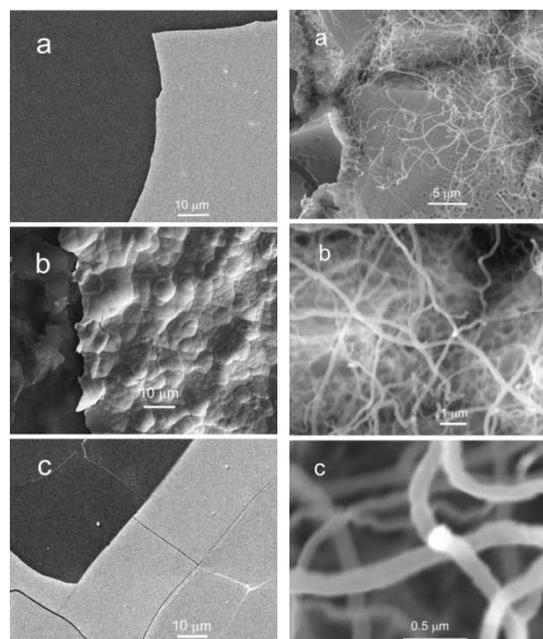


Fig.1

Fig.2

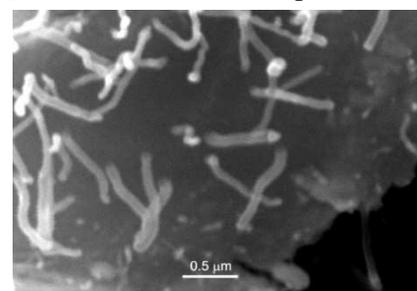


Fig.3

The influence of form release agent application to the quality of concrete surfaces

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The aim of this research was to test the quality of concrete surfaces in respect of form release agent application. Firstly, formworks were covered with the excess amount of form release agent without the cleaning by the soft cloth, secondly – form release agent was carefully cleaned, while the surface of the formworks became shiny. Concrete mixture's composition was selected randomly. The biggest attention was paid for the honeycombs and air bubbles of concrete surfaces. The research was made using different frameworks, such as: wood impregnated with polymeric oil; wood covered with rubber; sawn timber framework; plastic and metal. Various air bubbles of the concrete surfaces with the diameter of 1 to 8 mm were analyzed. The analysis was made based on the three concrete surfaces evaluation methods: CIB Report No. 24 "Tolerances on blemishes of concrete", GOST 13015.0-83 and the computer program – ImageJ. Also, the statistic of obtained air bubbles was calculated.

Keywords: *form release agent, concrete surface quality, pores, honeycombs, concrete surface evaluation methods.*

Topological Methods For Estimation Of Technological Properties Of Quartz Raw Materials

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In present time most of prospecting works and feasibility studies of quartz deposits are based on technological criterions. There is no express method to define high potential deposits.

Stereometric (topologic) estimation of intergrowths boundaries of mineral individuals in combination with others characteristics helps to obtain completely full information about ontogeny of mineral aggregate. Further based on this information it is possible to find best ways and methods of rock and raw materials disintegration, also to find new perspective deposits of quartz raw material. Results of quantity analyses are the best base for developing of fabric-genetic classification of rocks and technological scheme of mineral processing.

Study of surface singularities of quartz aggregates with a help of ontogeny analysis gives valuable information about quartz body formation. Formation and retransformation conditions reflect in raw materials properties. Investigations on early stages of geological-prospecting works give new possibilities to define optimal technological types before exploration works begin. Addition of results of this methodic to technological process of glass production helps to increase of research intensity and to decrease the total expenses to take high quality products.

Keywords: *quartz raw material, ontogeny analysis, surface properties, technological types of quartz raw material*

Session 4.

Hetero-Modulus and Hybrid Materials

Effect of SrO on the microstructure of calcium zirconate

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Binary phase diagram CaO-ZrO₂, where CaZrO₃ is only one compound, has been constantly in interested in many scientific area. Valuable properties of CaZrO₃ like high melting point (2345°C), thermal shock resistance, high dielectric constant, practically pure oxygen ionic conduction, electrical conductivity, high strength and excellent corrosion resistance against alkali oxides allows its use in a wide range of application and various forms. Both, in pure or in modified form offer great opportunities for its use, such as: fuel cells, filters, sensors, solid electrodes, oxygen probes, membranes and multilayer ceramic capacitors. Doping of CaZrO₃ with some trivalent cations showed appreciable protonic conduction in hydrogen containing atmosphere and doping with some oxides caused oxygen ion conductivity.

Stoichiometric calcium zirconate and calcium zirconate with 10 mol.% SrO were prepared by a solid state reaction. Pure chemical calcium carbonate and zirconia, in stoichiometric amounts, were used as the starting materials in the synthesis of pure CaZrO₃ powder. Also were used reagents as SrCO₃. Samples were obtained by firing a two-stage in 1200°C and 1700°C.

The aim of this work was observed the microstructure and estimate the influence SrO on the sinterability. XRD analysis was used to determine phase composition. Samples were tested by using mercury porosimeter. For microstructure analysis SEM/EDS method was used. By applying the appropriate oxide as SrO can modify the microstructure and properties of sintered calcium zirconate.

Estimation of mathematical expectations and fluctuations of thermoelastic fields in heterogeneous mediums

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Seismotectonical reaserch

For solving a wide range of problems in mechanics of heterogeneous mediums, it must be based on the theory of random functions. This work studies a multiphase thermo-elastic stochastic inhomogeneous medium in which each phase is described by Duhamel-Neumann law with its elastic modules and thermal stress coefficients. This medium is described by means of the common system of motion equations and thermal balance. In this medium the elastic modules, thermal stress coefficients, stresses, deformations and temperature will be random functions of coordinates. Random function can be represented as the sum of mathematical expectations and fluctuations. The purpose of the research is to build the system of equations for mathematical expectations of deformations and temperature as well as to estimate the influence fluctuations of the elastic field on behavior of the medium. For most mediums this problem is difficult and it can hardly be solved in the general case. However in particular cases the averaged equations can be found. In the correlative approximation, ie when physical characteristics of the phases differ slightly, the averaged equations will be the same as the initial equations with effective thermoelastic parameters. In this research the method of finding these parameters and the method of estimating of fluctuations of stress in the two-phase thermo-elastic stochastic heterogeneous medium were developed. The second type of mediums in which the averaged equations can be developed are layered media. If in the averaged system of the equations the Laplace transformations are made and the effective thermoplastic parameters are found, these parameters will depend on the parameter of Laplace transformation. This means that the law Duhamel-Neumann appears a new term with the time derivative of strain and temperature.

Hetero-Modulus and Hetero-Viscous Alumina Matrix Composites with Extreme Dynamic Strength

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Examining the material structures and behaviours of different ceramic bodies and CMCs under high speed collisions in several years [1, 2, 3] 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 reinforced with Si₃N₄, SialON and AlN submicrone and nanoparticles new corundum-matrix composites have excellent dynamic strength during collisions with high density metallic bodies having speeds about 1000 m/sec or more. The reason is that in the alumina matrix composites a phase transformation of submicrone and nanoparticles of alpha and beta silicone-nitride crystals into cubic c-Si₃N₄ diamond particles can be observed [4] when the high speed collision processes with high density flying metallic bodies are taken place in vacuum or oxygen-free atmosphere.

Using the energy conception of collisions, the energy engorgement by fractures, heating and phase transformations are described by the authors, as well as mechanical stress relaxation processes in the hetero-modulus and hetero-viscous composite materials after the high speed collisions with high kinetic energy flying objects.

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: alumina, collision, composite, diamond, dynamic, hetero-modulus, silicon-nitride, strength.

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High Porosity Alumina as Matrix Material for Composites of Al-Mg Alloys

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The sophisticated industry and technologies require higher and higher assumptions against mechanical strength and surface hardness of ceramic reinforced metal alloys and metal matrix composites. Applying the well-known alumina powders by dry pressing technology and some special pore-forming additives and sintering technology the authors have successfully developed a new, high porosity alumina matrix material for composites of advanced Al-Mg alloys. The developed new matrix material have higher than 50% porosity, with homogenous porous structure and pore sizes from few nano up to 2-3 mm depending on the alloys containments. Thanks to the used materials and the sintering conditions the authors could decrease the wetting angles less than 90° between the high porosity alumina matrix and the Al-Mg alloys.

Applied analytical methods in this research were laser granulometry, scanning electron microscopy, and X-ray diffraction. Digital image analysis was applied to microscopy results, to enhance the results of transformation.

Keywords: *porus ceramics, alumina, wetting angle, matrix materials, composites*

Hydratization of Cement Clinkers in Carbon Dioxide Medium

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The cement is indispensable in the building industry as hydraulic binding material. Calcium-hydroxide and calcium-silicate-hydroxides form during the hydration of cement. The aim of this study is present a new aging reactive process in carbon-dioxide medium. Calcium-carbonate and water arise from the result of the reaction of carbon-dioxide and the calcium-hydroxide developed in hydration. Owing to the accelerated carbonization of the free lime a new material structure built up. The changes in the mineral composition and in the crystal structure were examined. By the description of the chemical reactions of hydration process the carbonisation effects were explored. Cement probes were formed with three different water-cement ratio. The aging time was 28 days in carbon-dioxide medium. Beside the carbon-dioxide medium, the aging under water and in air were also performed. At the age of 1, 3, 7, 14 and 18 days, the comprehensive strength, the mineral content and the morphology were analysed.

Keywords: *cement, aging, carbonisation*

Influence of particle size distribution and volume fraction of mineral fillers on the rheological properties of asphalt mastics at temperatures between 60 °C–135 °C

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Bitumen–mineral filler composite materials (called asphalt mastics) are the most important components of asphalt concretes. These materials are responsible for the good cohesion between mineral aggregates and bitumen, and basically determine the properties (strength, stiffness) of asphalt pavements. In this research work the Authors examined the stiffening effect of two different types of mineral fillers (limestone and dolomite) used in asphalt mastics. Particle size distribution and volume fraction of fillers were chosen as influencing factors. Dynamic oscillatory tests were performed at temperatures ($T=60^{\circ}-135^{\circ}\text{C}$), linear viscoelastic parameters were determined and finally master curves of these material properties were generated at a reference temperature of 60 °C. Relying upon the complex modulus, phase angle and loss tangent master curves it was proved that due to the increase of grain size distribution and volume fraction the elastic properties of mastics will be dominated, therefore these fillers can improve the stiffness of mastics. The extent of stiffness was in all cases larger when limestone filler was used, than during the use of dolomite filler. The reason of this is the good cohesion and strong interaction between limestone particles and bitumen. In the knowledge of this, it is possible to design pavements that are less sensitive to rutting at high temperature. Keywords: mineral filler, asphalt, mastics, master curve, stiffness.

Investigation of the structure of multiwall carbon nanotubes in polymer matrix

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In the last ten years carbon nanotube composites are in the focus of the researchers. Concentration series were prepared using carbon nanotube containing masterblend by IDMX mixer. In the experiments polypropylene, polycarbonate and ABS polymers were used as matrix materials. The prepared materials were characterised by scanning electron microscopy. The carbon nanotubes can be seen on the fractured surfaces. We did not find any sign of agglomerates in the materials. The nanocomposites were investigated by LP-FTIR method. The specimens were irradiated with 1 W for 1 minute by CO₂ laser. The polymer matrix was burnt or charred by the CO₂ laser; the structure of the carbon nanotubes in the matrix was studied. The carbon nanotubes create a physical network in the polymers we used.

Improving physico-mechanics and structural properties of salted light cements by natural additions materials

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One of the most serious problems encountered when cementing casing in a well is the failure of the cement casing and cement formation bond. This is a major problem from the standpoint of allowing migration of fluids from one zone to another. Also, poor bonding can result in large losses of reservoir fluids, premature reservoir depletion, and unsatisfactory stimulation operations. With these factors in mind, it has long been recognized that superior cementing operations could be achieved if expansion could be induced in oil well cements. Expansion currently is induced in oil well cements by two methods, addition of salts (salt cements), or addition of other components.

This work concerns the elaboration of light salted cement with local materials for unconsolidated salt formations and the study of the expansion characteristics of light salted cements ...). Salted cements are used for cementing high salted area, which present little resistance to caving. Light materials could be used in combination with salt in order to solve this problem. This paper describes the properties and uses of cementitious mixtures containing 10 to 20% bentonite and 2% to 18% of saturated sodium chloride. Salt additions improve bentonite cements by increasing early strength and stabilizing viscosity without changing thickening time. The unique properties of salt in this type of system make savings of more 10% possible where light-weight, low strength cementitious materials is adequate to fill behind the pipe. The high water-free value tried to be solved by adding another natural light material : diatomaceous earth, which provide good cement slurry strength and low water-free content.

Further work deals with gypsum-Portland cement blends which possess good water resistance. Additional tests concern mechanical, rheological morphology and structural characterisation of this light cement. This study concerns natural material combinations in which a normally total accelerators exerts unique partial properties. Utilizing these limited effects improves light cements.

Keywords: *cementing, expansion, salt formation, light cement, natural adding, salt, bentonite, diatomaceous earth, gypsum, mechanical properties, structural characterisation, morphology*

Nano-architecture Control of Hybrid Materials for Advanced Pressure Sensors

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Nano-architecture controlled organic-inorganic hybrid materials consisting of elastomeric polymer matrix and conductive/non-conductive nanoparticles have been designed and developed to utilize them as advanced pressure sensor devices. The sensing mechanism is based on the dynamic variation of percolation structure of conductive phase during the deformation of hybrids, which implies that the controls of percolation structure of dispersed conductive phase as well as dispersing nano-fillers are the key technology to achieve better sensing performance¹. In this research, we have attempted nanocomposite technology based on low-viscous solution mixing processing to develop high-performance and low cost pressure sensor materials.

When micro-sized conductive inorganic platelets and nano-sized clay particles were dispersed to elastomer, stable pressure sensing could be possible. However, their performance was strongly influenced by the mechanical properties of micro-sized platelets, which were often broken during loading and unloading sequences. To obtain better sensing and mechanical properties, nanosized carbon and inorganic nanoparticles such as clay and silica were used as the conductive and strengthening fillers, respectively. Organic solvent was used to mix them with silicone pastes homogeneously. Special emphasis was placed to immobilize organic surfactant onto the silica nanoparticles to obtain hydrophobic surface. Electrical resistivity of the hybrids could be controlled by the amount of nano-carbon, and its percolation threshold was found to be around 1.6 vol.%, which was much lower than that of micro-sized inorganic platelets (~8 vol.%). Applied force – electrical resistance (FR) relations were measured to verify sensing performance. It was found that high repeatability of FR curves during cyclic compression up to 20 N/cm² could be achieved when nano-sized SiO₂ was modified by silane coupling agents, showing that this kind of nano-hybrid materials are the promising candidate as flexible, high-performance and low cost sensors applicable for human-interface systems, artificial skins and so on.

In addition, another nano-hybrid technology has also been attempted to develop novel pressure sensor materials by synthesizing nanosized polyaniline (PANI) particles and dispersing them as the conductive filler to silicone elastomer. As expected, pressure sensing performance was achieved. Detailed nano-architecture design and development as well as their sensing performance will be discussed.

Keywords: *pressure sensor, hybrids, nanocomposites, percolation, nanocarbon, silica, surface modification, force-resistance*

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New Advanced SiC Ceramics Based on Natural Biomaterials

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On the basis of several years experiments in investigation of hetero-modulus material structures and using natural biomaterials and high purity quartz powders the authors successfully developed new high porosity low density SiC ceramic cellulars and foams.

Because of the high values of melting temperatures and elastic modulus the borides, nitrides and carbides have accentuated attentions in development of high mechanical and thermal performance ceramics and composites. Among of them the silicon-carbides (SiC) have a particular interest because of their high melting temperature (~2700 °C) and Young's modulus (~510 GPa) and excellent chemical resistance.

For the development of new silicon-carbide and carbon-silicon-carbide (C/SiC) cellular ceramic composites and foams the author used high purity SiO₂ powders mined in Fehervarcsurgo (Hungary) and a biomaterial reagents made from renewable vegetable under trade-name IG-R1. These low density high porosity silicon-carbides probably can be successfully applied in development of light weight ceramic reinforced metal alloy composites in the future. The structure and XRD analysis of used raw materials and the achieved by authors new SiC and C/SiC ceramic composites and foams are described and shown in present work.

The aim of the authors is to establish a new technology for producing the widely used silicon-carbide, which allows the production of silicon-carbide foam with nearby and easily available materials.

Keywords: *biomaterials, ceramics, C/SiC composites, foams, hetero-modulus, SiC*

New galvanic technology for making of hybrid metal ceramics coatings

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Technology allows to get galvanic powder metal ceramics coatings with particles of the second component. As basis of material matrix of coating can be using metals: Ni, Co, Fe, Cr. As additional component in coating may to use fine- or ultra-dispersed powder material or powder ceramics, for example SiC, B₄C, BN, B etc. This decision allows to a great extent to reinforce the matrix of coating, because particles of additional component consolidate and reinforce composite. Technology allows to plate powder-like materials on the basis of carbides (WC, TiC, B₄C and other) and diamond powder-like materials of different dispersion at using metals Ni and Co as basis of coating.

Coatings of powders including its particles of different sizes, for example, combine in one volume micro- and nanoparticles. Coatings indicated the efficiency for conditions of contact points at mechanical interoperation as friction units or as segments of the instrumental application. At such structure microparticless perceive on itself the basic loading, nanoparticles to reinforce the matrix of coating. It all increasing the mechanical properties of composition material.

Technology is computer-assisted and allows to use the pulse current in the technological process at obtaining of galvanic powder coatings. It allows to create the finedispersed structure of matrix of coating with high mechanical properties and highest concentration of nanoparticles as additional phase in a matrix body.

Technology can be effectively using:

- as the first stage of electric technology with the purpose of making of instrumental materials at the use of methods of consolidation of powder-like materials under electric current action (Electro Discharge Sintering Technology(EDS), Spark Plasma Sintering Technology (SPS)).
- for strengthening or renewal of details for machines and mechanisms which can to operate under conditions of mechanical contact interoperations.

Keywords: *galvanic powder metal ceramics coatings , segment of the instrumental application, pulse current , electric technology, Electro Discharge Sintering Technology, Spark Plasma Sintering Technology*

Making Silica-Carbon Nanotube Composite Materials for non-linear Optics

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Carbon nanotubes (CNT) have been widely investigated by researchers to improve understanding of the unique electric mechanism and optical properties [1]. Semiconducting, single-walled carbon nanotubes (SWCNT) is a promising material for saturable absorbers in laser mode locking [2] because of the fast recovery time, which covers a broad spectral range in the near infrared, and excellent chemical stability. Furthermore, SWCNT-based saturable absorbers can be fabricated by simple and economical methods, such as spray, spin coating [3] or horizontal evaporation methods [4].

However, application of those techniques requires dissolution of CNT's. Unfortunately, CNTs are insoluble in any solvents and forming bundles due to strong van der Waals interactions that tightly hold them together. CNT's insolubility decrease the overall yield of usable material and interfere with most of the desired properties of the CNT's [5]. Better CNT solubility can be reached via chemical covalent or non-covalent modification of tube surface. The use of various surfactants and polymers can highly increase solubility of CNT in polar and non-polar media.

Currently, fabrication of CNT and polymer composites for saturable absorbers is very popular. But due to nature of organic polymer matrix, these composites are unstable on higher temperatures or in high energy light expositions. Therefore a sol-gel process for the fabrication for inorganic (i.e. silica) or semi-organic (organic-modified silica) matrix can be a promising way to produce photo-chemically and thermally stable CNT composites: thin/thick coatings, glasses and ceramics

The aim of this work - using spin-coating technique make a SWCNT's and silica composites. So foremost SWCNT's solubility in ethanol was investigated using different surfactants – Triton (X-100 and X-305), polyvinylpyrrolidone (PVP 360 000M and PVP 24 000M) and Poly(4-vinylpyridine) (P4VP 40 000M). Most stable colloidal solution was obtained using a P4VP as surfactant – solutions were stable up to 6 weeks. Therefore this surfactant was used for the fabrication of SWCNT/Silica composite coatings. Tetraethyl orthosilicate (TEOS) was used as silica precursor and using base catalysis colloidal silica nanoparticles was formed. SWCNT's was directly dispensed in a colloidal silica sol and coatings made by spin-coating technique. All samples were investigated under optical, atomic force microscopy methods, and optical non-linearity was measured.

Keywords: Carbon nanotubes, Silica, non-linear optics, saturable absorber

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Materials Design of Functionally Graded Ultra-High Temperature Ceramics Based on “Ridge-Effect” Phenomenon

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The practical experience collected from the numerous tests of thermal protection systems in aerospace technologies shows that the application of monolithic as well as multi-phase ceramics, e.g. based on the refractory boride – SiC systems, is very limited, because of its weak thermal-shock resistance. The only materials, which are used currently in aerospace practice, are carbon-carbon composites. However, all numerous attempts to improve oxidation resistance by covering the surface of these composites with various protective coatings were fruitless, because the adhesion between the coatings and substrate does not meet the necessary requirements. This general problem in materials design for ultra-high temperature applications can be solved by the replacement of carbon matrix by the high-modulus refractory carbides, such as TiC, ZrC and HfC, which demonstrate extremely high thermal strength being combined with various particulate and/or fibrous low-modulus graphene-like carbon structures. The knowledge of recently discovered, temperature-pressure-dependent phenomenon, 'ridge effect' allows preparing protective self-sintering/self-healing oxidized scales on the surface of carbide-carbon ceramics to inhibit considerably high-temperature corrosion/erosion of the material. The excellent adhesion of the functionally graded scales is provided by the intermediate carbon-doped oxide and oxycarbide layers. By means of the pre-oxidizing technique it becomes possible to convert outer layers of the carbide matrix into oxide phases without any damage to the carbon reinforcement of hetero-modulus ceramic composites. Thus, the discovery of 'ridge-effect' becomes the milestone in the development of high-temperature materials and opens new horizons for the design of next generation of thermal protection in aerospace and nuclear engineering.

Peculiarities of Mechanosynthesis Carbides and Borides of Transition Metals

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There is much information on mechanosynthesis of refractory compounds. However, no regularities of formation of refractory compounds through mechanosynthesis have been established yet. The aim of the present work was to study structural transformations under milling of IV and VI group metals, such as Ti, Zr, Hf, Mo, and Cr, in a planetary mill (AIR-015M) in the presence of non-metallic additives, such as carbon and boron. To make the structure parameters more precise, the full-profile Rietveld method was used to adjust the calculated dispersion profiles to the experimental ones from the corresponding crystalline phases. For comparison, the IV group metals Ti, Zr, and Hf, which have a *hcp* lattice, and the VI group metals Cr, Mo, and W, which have a *bcc* lattice, were selected.

Milling of the IV group metals powders with boron and carbon yielded abruptly the following substances within a very short milling time: TiC, TiB₂, ZrC, ZrB₂, HfC, and HfB₂. Titanium and zirconium carbides could be obtained within 12 min milling, and borides of titanium and zirconium within 7 min. Basing on the diffraction patterns and interpretation of them using the Rietveld method, we can suggest the following scheme of structural transformations of IV group transition metals under milling with boron or carbon: at the initial stage of milling, carbon penetrates into the metal lattice and forms interstitial solutions, whereas boron forms substitutional solutions and initiates significant distortions and stresses. On reaching certain limit stresses, a phase transition occurs via collective movement which results in relaxing the stresses and forming new phases (TiC or TiB₂) with slight lattice distortions. This kind of phase transition is possible in the case of diffusionless transitions in dense-packed structures characterized by the correspondence of structure elements in the initial and final phases. In our case, there is such a correspondence between the Me (002) → MeC (111), and Me (002) → MeB₂ (001) planes. The transition Me → MeB₂ leads to the formation of phases with a high coefficient of space occupation.

The transition VI group metals Cr and Mo have a *bcc* structure. Milling of chromium-carbon mixtures within 90 min in a planetary mill can produce nanoparticles of the single-phase Cr₃C₂ through amorphization of the initial components. Mechanosynthesis in the Mo-C system yields the formation of a mixture of the MoC and Mo₂C carbides. A mixture of the borides CrB₂, CrB, and Cr₅B₃ is obtained upon milling powders of chromium and boron in a planetary mill. The formation of a large number of phases in the synthesis of molybdenum carbides and chromium borides is evidence of the nucleation mechanism of their formation.

Hence, by milling of powders of transition IV group metals, which have a *hcp* lattice, with carbon and boron in a planetary mill, one can create conditions for the formation of nanosized distorted powders of solid solutions due to shock loads and shear deformation and their subsequent crystallographic transformation through collective movement. This leads to the formation of structures with the highest packing density, namely MeC and MeB₂.

Under milling of transition VI group metals with carbon or boron in a planetary mill, formation of compounds occurs through the formation of nuclei of a new phase.

Keywords: *mechanosynthesis, carbides and borides.*

Synthesis and Characterization of MgAl₂O₄ Nanopowders by a Reverse Micelle Processing

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MgAl₂O₄ nanoparticles was synthesized by reverse micelle processing the mixed precursor (consisting of Al(NO₃)₃ and Mg(NO₃)₂). The Mg ferrite was prepared by mixing the aqueous solution at a molar ratio of Mg : Al = 1 : 2. XRD pattern show that the crystalline phase of the synthesized particles with heat treatment 500°C for 2h is spinel. The average size and distribution of synthesized powders were in the range of 10-20nm and narrow, respectively. The average size of the synthesized powders increased with increasing water to surfactant molar ratio. The XRD diffraction patterns show that the phase of MgAl₂O₄ was spinel (JCPDS no.22-1012). The synthesized and calcined powders were characterized by thermo gravimetry- differential scanning calorimeter (TG-DSC), X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM). The effect of synthesis parameter, such as the molar ratio of water to surfactant, is discussed.

Keywords: MgAl₂O₄ , Nano Powders, Reverse Micelle Process, Refractory

The Analysis of an Innovative Wooden Folded Slab Behavior

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Wooden slabs that employ folded structures have a better behavior in terms of rigidity in comparison to traditional wooden slabs, an aspect of great importance in respect to a light structure. The few examples of wooden folded slabs in production today utilize joined board elements to form a folded structure for the inner layer of a wooden sandwich slab panel where the faces are the ceiling and the floor boards. The slab panel proposed has an inner layer made of a composite with cork particles and fiber glass in a polyester matrix that can be molded into a folded shape with a spray-on procedure. The composite material combines fortunately the mechanical qualities of fiber glass with those of a light and sustainable material: cork. Cork particles are an ideal choice as part of a composite material, because they are environmental and better suited for thermal and acoustic damping than other natural or synthetic materials. The article presents an analysis of the innovative wooden folded slab panel and a comparison between this innovative structural solution and one made up of boards, already in production, in terms of economical and structural feasibility. The aim is to investigate if the hybrid composite with cork particles, E-glass fibre and polyester resin is, according to the results of the analysis, a viable solution for folded slabs.

Keywords: *cork, folded slab, rigidity, wood composite*

The Effect of Microstructure on the Local Wear Behavior of Dual Phase Steels

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For experimental purposes we used a micro-scale ball-cratering tribometer. In case this test, the process parameters (load, angular speed) were constant, the solution of the wear-kinetic differential equation could be expressed in a simple, closed form. It was tested four types of samples according to the next microstructure, low martensitic steel sample (25% martensite and 75% ferrite), medium martensitic steel sample (50% martensite and 50% ferrite), high martensitic steel sample (70% martensite and 30% ferrite), full martensitic steel sample (100% martensite).

It is known that the friction and wear properties of metals and alloys show a strong correlation with their chemical composition, hardness and microstructure. The aim of this work was to analyse and evaluate the correlations between the microstructure and the wear properties of different dual phase steels during dry friction.

Keywords : *local wear, microstructure, dual phase steel, wear coefficient*

Session 5.
**Light Weight Materials with Predesigned and
Controlled Nanostructures**

Alumina with different porosity and the crystallites sizes

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The structure and mechanical properties of alumina ceramics based on powders with a different grain size has been investigated. It was found that increased amount of nano- Al_2O_3 powder is accompanied by a change of the compaction mechanisms material with increasing sintering temperature. Determination of the activation energy of grain growth process during sintering showed that the main mechanism of sintering is a grain-boundary diffusion.

It is shown that increasing of nano- Al_2O_3 powder content in the mixtures leads to changes the pore structure in sintered ceramics from a high-porosity ceramic skeleton with a well-developed system of channel-forming pores to ceramics with isolated pores. The change in the pore structure was observed for 50% porosity and caused an increase in the level of crystal lattice microdistortions. The changing character of the pore structure is accompanied by a violent decrease in strength, which corresponds to the percolation transition in this ceramic.

A correlation between the microstresses in the crystallites and in the sintered ceramics macrostresses, at a minimum microstrains corresponds to the strength of 500MPa, and microstresses 2.5 MPa correspond exactly to the macro softening material.

A New Versatile Route to Ceramic Thin Films on Plastics: A Solution-Based "High-Temperature" Processing

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Large area metal oxide thin films on plastics are strongly demanded in flexible electronic device technologies as well as in technologies that aim at replacing glasses by lightweight plastics. Many of the active functions of oxide thin films emerge in their crystalline states with high bulk density or small porosities. Crystallization as well as densification, however, is driven in principle by atomic diffusion at high temperatures where plastics cannot survive. This is why great efforts have been made for over thirty years to develop "low-temperature" deposition techniques, most of which are vapor phase depositions, and how to crystallize and densify the films without "firing" has been focused on. Here we report a totally different route that guarantees crystallization and densification by firing. The technique comprises (i) the deposition of an organic or carbonaceous release layer on a thermally resistant substrate like silicon, (ii) the deposition of the precursor gel film by spin- or dip-coating, (iii) the conversion of the gel film into a crystalline oxide ("ceramic") film by firing, and (iv) the transfer of the crystallized film onto a plastic substrate using a thin layer of adhesive. Although ceramics are brittle materials, cracking could be perfectly avoided by suppressing the severe bending of the plastic substrates on the transfer process. The crystalline oxide thin films thus obtained on plastics were ca. 90 - 700 nm thick, crack-free and transparent, exhibiting flexibility, which implies the potential of the technique to be applied to high throughput roll-to-roll processes. We realized optically reflective anatase films, and electrically conductive indium tin oxide films on plastic substrates. Even crystallographic orientation and patterning were demonstrated to be achieved for crystalline zinc oxide films on plastics.

Keywords: *Plastics, Ceramic thin films, Coating, Sol-gel, ITO, ZnO, TiO₂, Flexible electronic devices*

Conductive, magnetic and structural properties of multilayer films

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Created due to the newest nanotechnologies nanosized magnetic materials display unusual characteristics: giant magnetoresistance etc. Multilayer films are widely used for instance as recording mediums of data with ultrahigh density, magnetoresistive random-access memory etc. This work is devoted to the research of influence of nonstructural characteristics to the conductivity and ferromagnetic resonance characteristics multilayer films of the series D1 - $\{[(\text{Me}1)_x(\text{Al}_2\text{O}_3)_y]-[\text{Si}]\}_{100}$, D2 - $\{[(\text{Me}2)_x(\text{SiO})_y]-[\text{Si}]\}_{100}$, E1 - $\{[(\text{Me}1)_x(\text{Al}_2\text{O}_3)_y]-[\text{Si:H}]\}_{100}$ where Me1 = $\text{Co}_{45}\text{-Fe}_{45}\text{-Zr}_{10}$, Me2 = $\text{Co}_{45}\text{-Ta}_{45}\text{-Nb}_{10}$, $0.3 < x < 0.62$, $3 < y < 12$, $y \approx 21-30x$, 100 – the number of layers. The films all series were obtained in an argon atmosphere and with addition of hydrogen (the E series). All films were deposited on substrates by the ion-beam sputtering method. The magnetic properties of films have been characterized by means of ferromagnetic resonance. The morphology, the phase surface nanostructure of films was studied with using of atomic force microscopy (AFM). Research of influence of metal phase concentration x and the width of nanolayers on FMC multilayer films has been carried out. For multilayer films composite-semiconductor wide maxima on the width of line FMR dependences on x are observed. The maxima of width of line correspond of maximum on thickness of semiconductor layer. The films of D-series are the best thread for using in the UHF data storing and processing devices at some x and thickness of semiconductor layers. For UHF absorbing materials the best are the films of D-, E-series. This work was supported by RFBR (grant 10-02-01327).

Keywords: *multilayer films, conductivity, magnetic properties, atomic force microscopy*

Effects of Calcination Parameters on Morphology and Photo-electrical Properties of Titania Nanotube Arrays

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Highly-ordered TiO₂ nanotube arrays were successfully prepared by electrochemical anodization in formamide based electrolyte containing 0.5 wt% NH₄F and 2 vol% H₂O at 30 V for 24 h. The effects of calcining temperature, calcining time and heating rate on formation of TiO₂ nanotube arrays were investigated in detail. The morphological changes and phase transformation of TiO₂ nanotubes were analyzed by X-ray diffraction, Raman spectrum, scanning electron microscopy and transmission electron microscopy. It is found that calcined temperature and calcined time determine crystal phase, while heating rate is only beneficial for crystallinity. The UV-vis diffusion reflection spectroscopy was used to examine the change of band gap energy. For application to dye sensitized solar cells, maximum conversion efficiency was achieved at 500 °C for 2 h with 10 °C/min heating rate, which is ascribed to the high anatase crystallinity and fewer surface defects of nanotubes. The optimum calcination conditions help to retard the electron recombination rate to increase V_{oc}, and allow higher dye absorption to increase J_{sc}.

Keywords: *TiO₂ nanotube arrays, calcination, dye-sensitized solar cells.*

Nanostructured Spray Dried Titanosilicate Microspheres – Structural and Surface Characterization

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Titania and silica attracted large amount of research due to their applications, especially in optoelectronics and photocatalysis [1, 2]. At the same time, their high chemical stability and non-toxicity [3] extended the research interest to the field of biomaterials [4].

Spray dried titanosilicate microspheres of less than 5 µm in diameter were calcinated between 700 °C and 1100 °C to induce in the amorphous matrices nanocrystalline phases. The microspheres belong to TiO₂-SiO₂ system, and their composition differs with respect to Ti/Si ratio of 1:2, 1:1 and 2:1. Anatase and rutile nanocrystals were developed by increasing the calcination temperature from to 1100 °C, and both are desired phases concerning their applications. Structural and surface characterization before interaction with biological and/or environmental media are an important issue for the expected behaviour in such media. The changes induced by the thermal treatments with respect to structure, morphology and Ti/Si ratio on the surface of the samples were investigated using thermogravimetical (TGA), differential thermal analyses (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Surprisingly, if for as prepared microspheres the surface atomic composition relative to Ti and Si is close to 1:1 ratio, the developed titania nanocrystals are covered with a thin layer of amorphous silica.

Keywords: *microspheres; nanostructures; titanosilicates; sol-gel; spray drying; XRD; SEM; XPS.*

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Please underline: **Oral** or **Poster** presentation

Magnetron sputtering of TiN-Si₃N₄ ceramic layers on textiles

Prof. Dr. Elzbieta Godlewska, Dr. Ryszard Mania, Dr. Krzysztof Mars

Hard ceramic layers are generally deposited to improve wear resistance of cutting tools. This paper deals with the deposition of composite layers of titanium nitride and silicon nitride onto Kevlar-type textiles. Planar magnetron with a pulsed power supply was used to produce ceramic layers by reactive sputtering. The sputtering targets were machined from titanium-silicon sinters containing up to 10 at% silicon. The sinters were obtained from elemental powders by a hot pressing technique. The films built of titanium nitride and silicon nitride, had nanocrystalline structure, as evidenced by Philips CM20 electron microscope. Thermal resistance of these layers on textiles, such as DuPont Kevlar and Nomex, was evaluated by a thermographic method. The incident heat flux density of 32 kW/m², corresponded to the heat source temperature of 6000°C, which is actually faced by fire-fighters in action. The measurements were continued to obtain the temperature of thermal shutter known as "pain threshold", being approximately 60 °C. Owing to the deposited TiN-Si₃N₄ layers, the time interval necessary to reach the 'pain threshold temperature' was remarkably extended. Keywords: magnetron sputtering, titanium nitride, silicon nitride, textiles.

**Microstructures and mechanical properties
of ultrafine-grained Al-Zn alloys**

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Annealed Al-30wt.%Zn and Al-78wt.%Zn alloys were grain-refined by two well-established severe plastic deformation (SPD) procedures: equal-channel angular pressing (ECAP) and high pressure torsion (HPT). The microstructures and the plastic behaviors of the SPD-processed alloys were investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and depth-sensing indentation. It was found that ultrafine-grained (UFG) microstructures were obtained by SPD in the investigated Al-Zn alloys. In addition to grain-refinement, the SPD-processing has also changed significantly the phase-composition of the alloys. Mechanical measurements revealed a close relationship between the enhanced strain rate sensitivity and the improved ductility of the UFG Al-30wt.%Zn which was attributed to grain boundary sliding and enhanced diffusion along the Al/Al grain boundaries in this alloy.

Thermoelectric properties of Bi- and Ag-doped magnesium silicide prepared by self-propagating high-temperature synthesis

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Magnesium silicide (Mg_2Si) doped with bismuth and silver was produced from elemental powders by self-propagating high-temperature synthesis (SHS) [1,2]. The reaction was carried out under dynamic vacuum in a dedicated laboratory set-up. It has been found that the grain size distribution of powder products is related to that of initial silicon powder. When silicon nanopowder was used in the synthesis, the resultant product was nanostructured. The particle size distribution of the powders was determined by Master Sizer 2000. Powder products were consolidated by Spark Plasma Sintering (SPS). Phase composition of the materials was examined by XRD, morphology and chemical composition by TEM/SEM and EDS. Netzsch LFA instruments were used for thermal property measurements. The Seebeck coefficient and resistivity were measured in the temperature range 25 – 630°C, using a home-made set-up. Thermoelectric properties of doped magnesium silicide obtained by SHS were discussed with reference to the synthesis parameters and dopant type.

Session 6.

Materials with Extreme Dynamic Strength

Ballistic Performance of Armour Ceramics on the Base of Alumina with Different Additives

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A main aim of the investigation was the improvement of the ballistic performance of alumina armour. It is considered key ceramics features in the providing of the ballistic performance are density, hardness, fracture toughness, bending strength, Young's modulus along with the structure of the ceramics [1-3]. Meanwhile, only optimal combination all of them can ensure required ballistic characteristics [4].

Consequently, several complex additives have been developed. The effect of these additives on mechanical properties and structure of corundum has been investigated. Complex additives were mixtures of oxides (MgO, MnO, Y₂O₃, SiO₂, TiO₂, ZrO₂) in different combinations and proportions. Commercial micron-scale α -alumina powder with median size of particles 1.8 μm was used during research. Pressed alumina specimens were sintered in air at the temperature range 1200-1750°C. Sintering samples were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results showed the possibility of alumina ceramics obtaining with high relative density about 99.2%, high hardness 18.0 GPa, high fracture toughness 4.15 MPa·m^{0.5}, high bending strength 560 MPa, high Young's modulus 450 GPa at 1650°C. At the final stage the ballistic performance has been estimated. The results are discussed and conclusions are made concerning optimal combination of ceramics features in the providing of the ballistic performance.

Keywords: armour ceramics, alumina, mechanical properties, ballistic performance.

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Can the topology of the carbon nanotube junction determine the mechanical behaviour?

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1. Molecular mechanical study was run on a set of carbon nanotube Y-junctions. In this set the structure of the Y-junctions had different topology: the heptagons at the centre of the Y-junctions were varied on different places. The results of the loading simulation processes show, that carbon nanotube Y-junctions having different topological structures behave different way. The places of the heptagons determine the mechanical behaviour during loading tests.

Keywords: *molecular mechanical, nanotube junctions, loading simulation*

Ceramics Based Light Weight Composites with Extreme Dynamic Strength

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On the basis of several years experiments in development of high performance technical ceramics [1, 2, 3] and in investigation of hetero-modulus materials and ceramic matrix composites [4, 5, 6, 7] the authors successfully developed a new family of ceramic reinforced hetero-modulus light weight composites with extreme dynamic strength. To obtain these light weight composites first were developed the matrix materials from different sort of sintered ceramics with different density and porosity, and after the prepared items were re-sintered using reactive sintering methods or were impregnated with nanoparticles of Si₃N₄, SiAlON ceramics or of light metal alloys having excellent mechanical strength and properties. Where it was necessary the pores and material structures of ceramic matrix materials anchored an excellent wetting for a wide range of light metal alloys, so the authors could develop several types of ceramics reinforced hetero-modulus light metal composites with extreme dynamic strength of different density. In this work the authors present the high density c-Si₃N₄ diamond particle reinforced corundum matrix composites and some of the specially developed low density ceramic foams and high porosity ceramic matrix materials for light weight metallic composites.

Analytical methods applied in this research for tests of material structure 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: alumina, collision, composite, density, diamond, dynamic, hetero-modulus, metal, silicon-nitride, strength.

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Fracture behaviour of TiC particles reinforced titanium matrix composites under fretting loading

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Titanium matrix composites with TiC particles have been tested under fretting loading in order to evaluate crack initiation conditions. Tests were performed with various particles rate, to estimate its impact on the nucleation, the propagation and the maximal length of cracks. In order to compare different materials, with different properties, all fretting tests were performed at the same maximal stresses, with the same contact geometry (cylinder on plane), and were interrupted at the same number of cycles. Furthermore, Amargier proved [1] that the radius of the cylinder had an important impact on the initiation crack condition. This is due to the stress gradient effect, induced by different contact width. As our materials have different properties, we had to apply different test conditions in order to have similar stresses distributions. Experimental results show the influence of particles rate: raising the rate involves a decrease of the initiation crack condition. Moreover, the increase of the particles rate leads to an increase of the maximal crack length. Finally, as the direction of extrusion implies a fibering of particles, results show the influence of the direction of the fretting loading, compared with this fibering direction.

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High and low-energy activations of nano-zirconia based systems

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It was shown that during mechanical activation zirconia-based nanosystem was divided into two subsystems with the average size of structural elements differing by two orders of magnitude. The fraction of the quasi-amorphous (X-ray amorphous) phase therewith increases. It was shown the ceramic was made up of linear grain chains with high bond strength at grain boundaries; in so doing, along with strictly linear elasticity the matrix exhibits micromechanical instability under deformation. In this case, the attainable strain and ultimate stress of ceramics produced from such powders greatly exceed the values for coarse-grained ceramics with similar parameters of the porous structure.

It was shown that microdamage accumulation has a threshold character and after local fracture the material is deformed by the previous law. There is direct correlation between macrostresses and local (meso-) parameters of strain distribution. The regions of uniform strain accumulation alternate with the regions where strains change abruptly, which leads first to local and then to macrofracture of the entire material.

Multiscale Modelling of Gradual Degradation in CMC with Application to TBC of Turbine Blades

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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, δ_{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. Application of the presented material model was done for modelling of TBC of turbine blades in jet engines. We assume that the turbine blade has protective covering (TBC) in form of thin ceramic layers. In the paper we discuss - using sub-modeling technique - the critical stress levels for degradation initiation and growth.

Keywords: *multiscale modelling of CMC, TBC coating of turbine blades*

Acknowledgement

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Tough hardness of the B₄C ceramics manufactured using submicron powder

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An effective approach to improve the physical-mechanical properties of advanced ceramics is making addition of nanoscaled powder to a matrix. The object of this work is investigation of influence of the submicron B₄C powder additives (up to 10 wt%) to commercial B₄C powder (M-5-P type, GOST 3647-80) on physical-mechanical properties of the ceramics produced by the spark plasma sintering (SPS).

Pulverizing of the commercial powder to the submicron fraction was carried out using the pneumatic circulating apparatus [1]. SEM-analysis (JSM-7500FA JEOL) has shown the mean size of the particles in the commercial powder of 4.7 microns, and it was 0.88 microns for the dispersed powder.

In the mixed powder B₄C_{mix} the submicron particles were uniformly distributed in a volume of the commercial powder owing to homogeneous mixing by the MT-2 mixer.

The sintering temperature (T_s) and pre-pressing pressure (P_p) at SPS were varied to optimize the sintering conditions for achievement of the greatest values of the density ρ , microhardness H_V and fracture toughness K_{Ic} .

The abnormal high values of the microhardness in B₄C_{mix} ceramics $H_V=47.9$ GPa and high density 98% have been achieved at optimal modes of SPS. In these samples the mean value of fracture toughness was $K_{Ic} = 8.0$ MPa*m^{1/2}. SEM-analysis of split images has shown that SPS technique under optimum modes allows to produce the dense B₄C ceramics with perfect grain structure and qualitative intergrain boundaries.

Keywords: *B₄C ceramics, spark plasma sintering, submicron powder*

References:

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Session 7.

Membranes - Science, Technology and Applications

Oxide-hydroxide zirconia-alumina porous ceramics and it applications for membranes

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It was studied the structure and phase composition of porous materials $ZrO_2 - Al_2O_3$, synthesized from alumina hydroxide and zirconia powder mixture. Zirconia powder were partly stabilized with yttrium oxide and produced by different methods.

It was shown that the increasing of the hydroxide content in the powder mixtures, for different producing method of ZrO_2 lead to the porosity volume increasing in the sintered materials. The sintering temperature increasing is accompanied by a reduction of the difference of porosity for composites with different content of alumina hydroxide. According to X-ray data the phase composition of $ZrO_2 - Al_2O_3$ ceramics is presented with the tetragonal and monoclinic phase of ZrO_2 , and high-temperature modification of alumina. In the composites based on ZrO_2 which was produced by chemical precipitation method the increasing of the sintering temperature is accompanied by a decreasing of tetragonal phase content of zirconia in the composites. In the composites based on ZrO_2 which was produced by plasma-spray method, the content of tetragonal phase is 90 % with sintering temperature increasing up to 1600 °C. It was shown that the content of ZrO_2 tetragonal phase increases with the increasing of alumina oxide content.

Oxygen permeation through dense BSCF ceramic membranes: sulfur contamination issues

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Fabrication of dense mixed-conducting membranes in the form of capillaries or hollow fibers provides superior surface-area-to-volume ratio compared to conventional planar or tubular membranes, making this geometry attractive for large-scale gas separation applications. For preparation of capillaries and hollow fibers by phase-inversion process, polysulphone or polyethersulphone are commonly used as binders. Formation of sulfates during sintering has, however, a negative impact on membrane performance. Although a possible solution involves adaptation of sulfur-free binders, another strategy to suppress the sulfur contamination impact may include tuning the rate-determining step of permeation process. The present work was focused on comparative analysis of oxygen transport mechanism through sulfur-free and sulfur-containing $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) membranes. Green capillaries were fabricated by phase-inversion spinning technique using polysulfone and cellulose acetate as binders for sulfur-containing and sulfur-free capillaries, respectively. Dried capillaries were crushed into powders, and disk-shaped BSCF membranes were pressed and sintered at 1373 K. Oxygen permeation measurements were performed at 923-1223K under air/(Ar+O₂) gradients; the microstructure of membranes before and after experiments was inspected by SEM/EDS. The relative roles of bulk ambipolar transport and surface exchange in the oxygen transport were analyzed. The presence of sulfates was found to decrease the permeation rate, mostly due to the partial blocking of surface oxygen exchange. A possibility to increase the oxygen flux through sulfur-containing BSCF membranes via surface activation up to the level characteristic of sulfur-free membranes was demonstrated.

Keywords: BSCF, ceramic membrane, sulfur contamination, oxygen permeation, capillary, hollow fiber, surface exchange

Session 8.
Minerals for Environmental and Medical
Application

Analcime-bearing rocks as perspective sorbents

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Last decades zeolites and zeolite-bearing rocks attract steady interest. One of the types of zeolite raw materials – analcime-bearing rocks – is widely spread in Timan and Timan Region (Komi Republic). By the properties analcime concedes wider porous zeolites, such as clinoptilolite and mordenite. However, the association of analcime with clay minerals, which also possess ion-exchange and sorption properties, allows considering the given rocks as sorption raw material of mixed composition.

It is determined that purification of waters by means of analcime-bearing rocks is effective by many indexes: sorption capacity of iron ions 0.13 mg-equiv/100 g /100 g, amines 10 mg-equiv/100 g /100 g, magnesium 5.94 mg-equiv/100 g /100 g, phosphates 1.42 mg-equiv/100 g /100 g. Rather high adsorptive properties are assumed in relation to oil products and PVAC [1]. By the characteristics the analcime-bearing rocks from Timan can be applied as a filtering material for the purification of household-potable water in fast filters in water intake structures instead of quartz sand. (Analcime-bearing rocks were compared to quartz sand, and not to other sorbents, for example zeolites, because now quartz sand is used at the local station of water purification.) The conducted experiments resulted in the assumption that both quartz sand and analcime-bearing rocks approximately equally improve organoleptic indexes of water quality (i.e. chromaticity and turbidity decrease). However analcime-bearing rocks much better reduces the content of iron (total) in water and reduces permanganate oxidability.

Besides, it is determined that analcime-bearing rocks are effective sorbents of radioactive elements (uranium and radium) from water solutions, where the concentration of radionuclides essentially exceeds sanitary-hygienic standards for potable waters.

This work was done under financial support of project 12-T-35-2055 of Earth Science program N5.

Keywords: *analcime, zeolites, analcime-bearing rocks, sorption, ion-exchange, water purification*

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Changes of colour and water-absorption of Hungarian porous limestone due to biomineralization

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Bacteria induced calcium carbonate precipitation nowadays is a widely examined process being a possible alternative for traditional stone conservation methods. Thus application connected, in situ experiments are recommended by researchers engaged in biomineralization. In our experiment methodology and materials developed by a French research group were applied on Hungarian porous limestone specimens, in situ. With the aim of obtaining homogenously, in-debt cured specimens, the samples were immersed into the liquid compound instead of spraying the curing solution onto their surface. Before and after the curing process, changes in water-permeability, capillary absorption, mass properties and color were measured, respectively. Since relatively low amount of solid material was applied on the samples, no significant changes were observed regarding the mass properties. Dry mass of the specimens increased with an average of 1,15%, and after soaking and drying the final value dropped to 0,23%. In contrast, the volume of water-absorption in the function of time decreased with an average of 5% m/m. As well, a significant decrease in capillary elevation was observed. After and during the treatment discoloration and changes in shade were noticeable. Degrees of color and shade-changes were observed both by using mathematical conversion of the images and image analyzing software.

Keywords: *biomineralization, Bacillus cereus, colour changes, water-absorption, porous limestone*

Clay Minerals: Adsorbophysical Properties

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The processes on a surface of clay minerals (kaolin, montmorillonite, etc) have an important scientific and practical value. On the surface the interrelation of processes at electronic, atomic and molecular levels is realized. Availability of mineral surface to external influences opens wide scientific and technical opportunities of use of the surface phenomena, so the research of crystal-chemical and crystal-physical processes in near-surface area of clay minerals is important.

After long term researches of gas-clay mineral system in physical fields the author has obtained experimental and theoretical material contributing to the creation of the surface theory of clays. A part of the researches is dedicated to studying the mechanism of crystal-chemical and crystal-physical processes in near surface area of clay mineral systems, selectivity of the surface centers to interact with gas phase molecules and adsorbophysical properties.

Photostimulated defect formation can reconstruct the surface of clay mineral systems, thus the oxygen of the gas phase becomes competitive in relation to mobile oxygen ions of the lattice at capturing energetically favorable positions. The influence of adsorbophysical fields on physical and chemical parameters of fine clay mineral systems is presented; it is caused by the connection of the adsorbed phase and volume at electronic, atomic and molecular levels.

The study of physical and chemical properties of fine clay minerals and their modification has a decisive importance for development of theory and practice of nanotechnologies: they are sorbents, membranes, ceramics and other materials with required features.

Keywords: *clay minerals, adsorbophysical properties.*

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Clay Minerals Deposit of Halakabad (Sabzevar- Iran)

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Clay minerals are expanded in south of Sabzevar. They are identified with light color in the field. The XRD and XRF chemical and mineralogical studies on the Clay minerals indicated that their main clay minerals are Kaolinite, Illite and Dickite. Pyrophyllite is minor clay mineral. Quartz and Sanidine non clay minerals are present with clay minerals. Ratio of Al₂O₃ is about 40 per cent, it is very good for industrial minerals. Volcanic rocks are origin clay minerals. Their composition are basic to acidic. In south of Sabzevar town there is a small part of these rocks available which include volcanic and volcanoclastic rocks. Geochemical and petrographic studies showed that their compositions are generally acidic and intermediates that have changed into clay minerals. Using the adsorption data, the reactions at the clay water interphase and the probable effects on the physical properties and structure of kaolinite are discussed. Pyrophyllite can also be used in the synthesis of ultra hard materials and as substituting material for talc in cosmetic and pharmacy industry.

Keywords: *Volcanic rocks- Kaolinite –Industrial clay minerals- Sabzevar –Iran*

Contribution to thermodynamic and kinetic investigations of Pb²⁺ adsorption onto acid-activated clay

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A sample of clay from Maghnia (N.W. Algeria) was chemically treated and characterized by powder X-ray diffraction, FT-IR spectroscopy and elemental analysis. The acid-activated clay (AAC) was used as adsorbent for Pb²⁺ ions from aqueous solutions by mean of batch experiments. The kinetic process was tested by applying pseudo-first order and pseudo-second order. The classic Langmuir and Freundlich sorption models and a dual-mode approach have been tested to study the sorption of Pb²⁺ onto AAC. Thermodynamic parameters ($\Delta H_0 = -7.22$ kJ/mol; $\Delta G_0 = -13.42$ kJ/mol) showed the adsorption of an exothermic process and spontaneous nature, respectively. Additional studies indicated that the acid-activated clay (AAC) selectively sorbed Pb²⁺ ions in the presence of competing ions Cd²⁺.

Keywords: Acid-activated clay (AAC), Removal, wastewater, Pb²⁺, Cd²⁺

Development of synthetic and natural mineral based adsorptive and filter media containing cyclodextrin moieties

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A long series of “emerging pollutants” has been discovered in the last decades which had not been known to be dangerous before. Most notable examples are “hormone disruptors”, some surfactants, pharmaceutical residues and metabolites which are present in minute, but still effective concentrations in both waste water and in natural waters. These “xenobiotics” are frequently not neutralized and removed by classical wastewater treatment methods and adsorptive media, as active carbon. As a part of a broader project a consortium of Hungarian companies, university departments and research institutes developed cyclodextrin based adsorptive and filter media for sampling waters containing xenobiotics and for reducing the xenobiotics content of wastewaters at the site of formation (e.g. in hospitals) or before consumption (e.g. in homes). This contribution presents a fraction of this R&D efforts: the development of polysilicate/cyclodextrin composites embedded into sintered polymer media and perlite based filter media with immobilized cyclodextrin on them. Chemical and radiation chemical methods of immobilization have been explored. The adsorptive properties of the filter media have been characterized by dye molecules and by selected drug molecules. The effects of synthetic conditions and material composition have been analyzed on the amount of active cyclodextrin sites and on the efficiency of immobilization on the support media.

Hydroxyapatite-based porous materials for heavy metal immobilization

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Hydroxyapatite minerals are well-recognized as some of the most efficient sorbents for heavy metal immobilization. This is due to their versatile and complex surface chemistry offering possibility for acid/base reactions, electrostatic interactions, ion exchange and dissolution/re-precipitation processes. Despite the large number of data already accumulated on this topic, an overview of the current literature indicate three main directions for improvement before real-scale applications can be foreseen:

(1) valorization of natural phosphates to decrease cost and environmental impact of the whole process. In this context, the use of available apatite minerals is limited by the limited porosity of natural phases. Although this may not be an issue for organics remediation [1], it strongly limits the rate of heavy metal immobilization. We will show here the easy conversion of natural phosphates into porous apatite phases with enhanced metal sorption properties [2].

(2) incorporation of organic moieties to increase the efficiency and, if possible, specificity of the sorption phenomenon. Although it is possible to introduce organic functionality within pre-formed apatite powders by simple adsorption or post-grafting strategies, we found that the direct incorporation of organic phosphonates [3] or calcium chelates (such as carboxylic acids) [4] during the step of apatite synthesis allowed a simultaneous control of the material porosity and surface reactivity. The presence of the organic function can greatly increase the apatite sorption capacities but it depends on the relative affinity of the considered metal for the mineral and organic component.

(3) elaboration of composite structures with improved stability or novel functionality. In particular, we have recently developed ZrO₂-apatite nanocomposites using the sol-gel technology [5]. These nanocomposites associate the microporosity of the Zr-phase with the mesoporosity of the phosphate particles. Moreover, these nanocomposites associate the respective good affinity of Cr(III) and Cr(VI) species for apatite and zirconia, respectively. Extension to other mixed apatite-metal oxide phases will also be discussed.

Keywords: remediation, heavy metal, porous materials, nanocomposites, hydroxyapatite,

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Leucoxene and TiO₂ photocatalysts for water purification

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The problem of effective water purification from organic compounds, bacteria and viruses is very serious. The currently applied technologies such as sorption, separation and destructive have several drawbacks, main among which is that substance-pollutants are transferred to a different location (for example, accumulate on the surface of the sorbent, which requires subsequent disposal). A possible solution to this problem is the use of photocatalytic method in which the oxidation of the polluting substances is due to dissolved oxygen in the presence of photoactive catalyst. As an active photocatalyst, we used a commercially available titanium dioxide, and leucoxene concentrate, as well as obtained using these materials titanium dioxide nanotubes. Some samples were modified with nitrogen.

Activity of the samples was studied by test reaction of photocatalytic decomposition of trichlorophenol. Samples with the highest nitrogen content were the most active. At the beginning of the reaction (time interval 0-30 min), the difference in the activity of samples were negligible. Presumably this moment corresponds to the accession of the OH⁻ group (formation of digidroksitrihlorobenzola). This is indirectly confirmed by the weak staining solution in a crimson color. As a result, the highest photocatalytic activity was observed when using the initial anatase (81%) and modified with nitrogen at a maximum temperature of titanium dioxide nanotube sample (88%). Photocatalytic activity of the other samples were identical (75-76%) and lower than that of anatase.

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Keywords: *leucoxene, anatase, titanium dioxide nanotubes, photocatalysis, water purification*

Nanocomposition sorbents obtained by mechanochemical synthesis for purification of service water

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One of the main parts of the general problem of environmental protection is rational use and protection of water basins. Improvement of sewage purification of methods will allow to reduce the volume of polluted water at industrial enterprises. The best way of rational usage of water resources is to improve the technology of purification of service water using effective adsorbing materials. Mechanochemical synthesis (MCS) used by us on the basis of one material, in particular quartz, allows to obtain substances with different sorbing abilities resulting from variation of the kind and amount of organic modifying additives as well as conditions of mechanical treatment. The particles of powder obtained by MCS are composition formations with a mineral nucleus and an elementorganic nanostructured shell with the thickness up to 100 nm, the composition and structure of which determine the sorbing properties of the material. Electron microscopic investigations showed the variety of morphological forms and nanostructured carbon formations on the surface of modified quartz particles. It is shown that the presence of carbon and iron complexes in the surface modified layer of a quartz particle allows to present the modified surface as a set of galvanocouples determining the sorption activity of the synthesized nanocomposition material. The presence of such nanosize galvanocouples on the particle surface can intensify the process of water purification from different elements dissolved in it that was verified by the results of experimental investigations.

The carried out investigations on purification of water by the adsorbent on the basis of quartz both in the form of powder and granules modified by MCS have shown that it provides a high degree of purification from organic compounds and heavy metal ions. It is shown that quartz material modified by mechanochemical treatment using different modifiers can be used both for selective and complex purification of water from different kinds of pollution.

Ferromagnetism of quartz powder developed due to mechanochemical treatment [1] allowed to create compositions differing in their adsorption, coagulation and magnetic characteristics which were designed for collection of oil spillages in natural water reservoirs as well as for purification of industrial sewage. Production of adsorbents with magnetic properties is of interest as their use will allow to increase the efficiency of oil collection followed by separation of oil products by the method of magnetic separation.

Keywords: *nanocomposites, quartz, modifiers, mechanical treatment, adsorbent.*

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Removal of phenols from water by use of layered double hydroxides

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This work is devoted to studies of processes of sorption of phenols by synthetic clay minerals of different composition.

Solving the problem of preventing contamination of the environment depends on the successful solution of the problem of industrial wastewater from pollutants, especially from phenols. Therefore becomes more urgent problem of pollution of natural waters, the growth in waste water and the search for effective methods of cleaning them.

The purpose of work is the search for new anionic sorbents. The application of this sorbent would allow to effectively remove of phenols from wastewater.

The most promising sorbents are sorbents based on double hydroxides of metals with the structure hydrotalcite. They are cheap, accessible and effective, universal sorbents, and they have a high absorption capacity, resistance to environmental stress and can serve as excellent carriers for fixing on the surface of various compounds with their modification.

The using of clay minerals with 2:1 structure type the changing value of the basal interlayered distances are very effective. Water molecules, as well as the positive and negative ions can be adsorb in interlayer space of these minerals. Therefore it is possible to place large ions between layers and forming columns. So we can create a system of pores where various small molecules can be placed. The pores size resulting in the intercalation process are about several tenths of nanometers. The samples were synthesized with the following ratios of cations in the matrix.

The specific surface of LDHs was determined by low-temperature nitrogen adsorption chromatographic method with subsequent processing of the results obtained by BET method.

The change of interlayer distance in LDHs after the adsorption of phenol, were investigated.

Adsorption capacity of the obtained sorbents was investigated in the reaction of phenols with LDHs different composition of general formula $Mg_xAl_y(OH)_z$ with varying degrees of isomorphous substitution. During the adsorption the amount of adsorbed phenol from the aqueous phase were fixed. The kinetic parameters of ion-exchange were studied.

Selective adsorption of Cd²⁺ ions from aqueous systems using acid-activated clay: Simultaneous effect of treatment and temperature

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A sample of bentonite from Maghnia (N.W. Algeria) was treated and characterized by powder X-ray diffraction, FT-IR spectroscopy and elemental analysis. The acid-activated bentonite (AAB) was employed as adsorbent for the removal of Cd²⁺ ions from aqueous systems by mean of batch experiments. The parameters that affect the Cd²⁺ sorption, such as contact time, solution pH, initial Cd²⁺ concentration, acid-activated mass of clay and temperature, have been investigated. The classic Langmuir and Freundlich sorption models have been tested to study the sorption of Cd²⁺ ions onto AAB. On the basis of Gibbs free energy ΔG_{ads} values range from -30.20 kJ/mol to -31.91 kJ/mol at 303.15 K to 333.15 K, the adsorption process is spontaneous nature.

Keywords: *Acid-activated bentonite, Removal, wastewater, Cd²⁺.*

The Effects of Mineralogical and Petrographical Features of The Lake District Rocks (Isparta, Turkey) on The Quality of Artificial Marbles

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Large quantities of marble blocks are produced from many new marble quarries which were opened up around Isparta and its surrounding region. The opened quarries are also affected negatively by weathering as a result of karstification. Therefore block efficiency of the quarries is low which results in a lot of waste materials will be used in cultured marble production. These waste materials are eliminated by using in production cultured marble. The production of artificial marble from marble waste materials around Isparta is main purpose of the study. The cultured marble is an attractive, healthy and homogenous building material. It has a wide application in the building sector. Artificial marble which composed of mineral dusts and polyesters has high mechanical strength, durable to various chemical and high temperature environmental conditions. Based on physico-mechanical properties, cultured marbles are convenient to Turkish Standards (TS). The materials used for the production of qualified cultured marble is directly related to the hardness of the minerals used as a filler in polyester. Physico-mechanical properties of cultured marble depends on physical properties of the filler minerals. The compressive strength of the cultured marble material is controlled by the physical properties of the filler minerals. Therefore the hardness of the cultured marble is determined by the hardness of the filler mineral. The following analyses; wet unit volume analysis, dry unit volume analysis, compressive strength of the materials, capillary water absorption analysis, analysis of seismic velocity (P wave) and the marble wastes bulk chemical analyses were investigated and the results of the these data evaluated and discussed on the cultured marble production with their respect to their physico-mechanical properties..In addition, natural and artificial marble were compared with respect to physico-mechanical properties. Many waste scrap materials are gathered on the agricultural lands which cause environmental pollution due to low efficiency of operations. For this reason, the cultured marble production has positive effect on environmental concerns by elimination of marble wastes as well.

Keywords: *artificial marble, polyester resin, marble quarry, compressive strength.*

Zeolite formation in a lead (Pb) polluted soil treated with fly ash and its implication in the environmental remediation

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Different remediation technologies have been developed in order to clean up contaminated soils and most of them use natural and synthetic zeolite as amending. In our study, zeolite X was directly synthesised in a soil artificially polluted by Pb, and the role of the synthetic mineral in the toxic element availability was investigated. A sample of soil artificially contaminated with Pb, was amended with fused coal fly ash and incubated for 1 year at about 30 °C. The coal fly ash was obtained from the ENEL thermoelectric power plant of Brindisi (Italy) whereas the soil was collected from an area near Potenza (Italy). The mineralogical, morphological and chemical composition of both starting materials were performed by XRD, SEM and XRF/ICP-MS analyses. The products were characterized by XRD, SEM/EDS and modified BCR three-step chemical sequential extraction.

The results obtained from our research show that zeolite X directly formed at low temperatures in the contaminated soil treated with coal fly ash. The crystallization of zeolite takes place readily after 1 month of incubation and amount of the newly-formed mineral increases during the entire 1-year-long incubation period. The presence of Pb does not interfere with the zeolite formation which, on the contrary, plays a leading role in the mechanism of immobilization of the toxic element. The SEM-EDX analysis shows that the toxic element is entrapped into the mineral, probably as hydroxide complex, and/or co-precipitated onto its surface. Although further investigations are in progress to confirm the speciation of Pb as hydroxide phases inside the synthetic zeolite, some literature data support this hypothesis. In fact structural analyses carried out on single crystal of zeolite X to investigate the Pb²⁺ behaviour in the zeolite strongly supports the hypothesis that [Pb(OH)]₄ clusters fully occupy the sodalite cages in hydrated forms [1; 2]. Our data also indicate that the Pb mobilization takes place only after zeolite structure is destroyed. This causes the availability of the metal previously entrapped in the synthetic mineral structure.

Keywords: *polluted soil, zeolite X, fly ash, environmental applications*

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Session 9.

Novel Synthesis and Processing Technology

Ceramic and Hybrid Nanocomposite Materials Based on Intercalated Layered Titanates. Synthesis and Application

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A wide field of nanocomposite materials design can be marked with a use of platelet nanoscale raw-materials which could be doped or/and intercalated with organic and inorganic ions or molecules as well as metal or semiconductor nanoparticles and organic polymers. This report is concentrated upon a synthesis of heterostructured nanomaterials based on platy nanoparticles of the hydrated potassium titanates intercalated with different molecules and cations or assembled with nanoparticles of other chemical composition and structure.

The parent hydrated potassium titanate (HPT) particles were synthesized by original low temperature molten salt synthesis and characterized with a lepidocrocite-like layered structure. The platy particles of the product had a diameter of 50-500 nm and a breadth of 5-20 nm. Due to a large interlayer distance (1.4-2.1 nm), the HPT particles were easy intercalated with different cations including d-metals cations ($\text{Me}^{n+} = \text{Ag}^+, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Cu}^{2+}$ and Cr^{3+}), cations of some organic dyes (methylene blue, rhodamine G) and cationic surfactants (CTAB, different amines). On the other hand, it was shown that the HPT platelets could be intercalated with some organic molecules such as dimethyl sulfoxide, porphyrines (methylpheophorbide-a) and organic polymers (polyvinyl alcohol, polyvinyl butiral). The intercalation process was realized in the corresponding solutions of water, alcohol, xylene or other organic solvents in the soft conditions at room temperature.

Another way to produce heterostructured particles was applied using the route of platy particles assembling. Some nanocomposites based on different combinations of titanate platelets with nanosheets (graphene, layered double hydroxides) or nanoparticles of another structure (astralene) were also produced.

The structure of the obtained nanocomposites was investigated using the TEM, SEM, EXAFS, DTA/TGA, IR and UV-VIS spectroscopy. The catalytic, electrical, optical, mechanical and magnetic properties of the obtained heterostructured nanopowders were investigated in the both dispersed and compacted forms.

The compacted powders intercalated with inorganic ions were compacted and thermally treated to produce ceramic nanocomposites. It was shown that the obtained products were represented with a nanocomposite ceramic structure consisting of the potassium hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$), hollandite-like $\text{K}_{1,34}(\text{Ti},\text{Me})_8\text{O}_{16}$ as well as MeTiO_3 , Me or Me_xO_y nanocrystals depending the chemical composition of the precursor material and conditions of the thermal treatment.

Taking into account some unusual and unexpected properties of the nanocomposite materials obtained by such processing technology, the potential directions of their technical application were analyzed.

Keywords: *layered nanoparticles, heterostructured materials, intercalation, assembling, compacting, sintering, nanocomposites,*

Fabrication and Characterization of $x\text{MgO}-y\text{Al}_2\text{O}_3-z\text{SiO}_2$ Powders for Crack Healing

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Hydrothermal processes have the potential for the direct preparation of crystalline ceramic powders and offer a low-temperature alternative to conventional powder synthesis techniques in the production of oxide powders [1]. This process can produce fine, high-purity, stoichiometric particles of single and multi-component metal oxides. Furthermore, if process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent are carefully controlled, the desired shape and size of the particles can be produced [2,3]. Nanosized $x\text{MgO}-y\text{Al}_2\text{O}_3-z\text{SiO}_2$ particles were prepared under high temperature and pressure conditions by precipitation from metal nitrates with aqueous potassium hydroxide. $x\text{MgO}-y\text{Al}_2\text{O}_3-z\text{SiO}_2$ particles were obtained in the temperature range of 190 °C ~230 °C after 6hours. TEM and X-ray diffraction patterns showed that the synthesized particles were crystalline. The average size and size distribution of the synthesized particles were below 50nm and narrow, respectively. The effects of synthesis parameters, such as the solvent ratio of starting solution, pH of starting solution, reaction temperature and time, are discussed

Keywords: $x\text{MgO}-y\text{Al}_2\text{O}_3-z\text{SiO}_2$, Nano Powders, Hydrothermal Process, Crack Healing

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Formation of Nanostructures in Brittle Materials with Transformations

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Transformation-toughened MMC show much promise for being applied in heavily loaded units. It should be noted that there are currently no sufficient data on the behavior of such materials at high mechanical loading and the main emphasis is now put on studying the material behavior. The present paper is aimed at studying mechanical behavior and structural phase state of TiC-TiNi and WC – Hadfield steel composites in different kinds of loadings.

It was shown that in conditions far from transformation the binder in MMC was deformed by dislocation glide as an ordinary crystal. In this case yield stress is inversely proportional to the carbide spacing, in alloys with high solid phase content it is not achieved up to fracture. Fracture of the material is catastrophically brittle. Deformation tests of composites near the phase transition temperature show that there are different transformations induced by a highly non-uniform stress state of the binding phase. Under loading it was found in the binding phase the formation of a nanocrystalline, highly disoriented structure with the characteristic size of crystallites less than 10 nm. This material has high plasticity and hardening. It governs an efficient transfer of external load to solid particles, inducing dislocation glide even in typically brittle titanium carbide particles. The physical meaning of using binders with unstable structure in composites involves a decrease in the scale of the structural level of plastic deformation due to the formation of the micro-, and nanocrystalline structure of the binding phase during nonuniform loading.

Out-of-furnace synthesis of high-temperature ceramic materials in the revolving reactor

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Optimization and increase in the economic effectiveness in the aluminothermic production processes is directed toward obtaining of two finished valuable products - metal and oxide material [1]. The purpose of the research is an increase in cleanliness and quality of the obtained crystalline phases due to the application of centrifugal acceleration during entire period of interaction of initial components.

The out-of-furnace synthesis of clean artificial minerals with the high abrasive properties also of refractory ceramic materials is investigated. Electric pulse excites exothermic reactions in the mixture of initial components at the same time in three reactors fixed on the rotation shaft. The wave of combustion is propagated along the axis of cylindrical reactor [2]. Rate of combustion is connected with the frequency of rotation. Experimental installation makes it possible to increase the starting value of centrifugal acceleration to 2 000 g. The temperature in the wave front reaches 2 500 K. The materials of the assigned phase composition are formed from the fusion. Admixtures are derived from the structure as a result of a difference in the density.

Corundum and solid solutions on the basis of corundum are synthesized. The possibility of regulating the concentration of the solid solutions of chromium in the crystalline oxide of aluminum by means of a change in the centrifugal acceleration is shown. Alumo-magnesium spinel and alumo-cobalt spinel of the high purity are obtained. The Mullite and mullite- corundum mixtures with different relationship of crystalline phases are synthesized.

Microstructure and physical properties of the obtained materials are investigated. Artificial minerals showed their competitive ability on the hardness with respect to the natural analogs and to those obtained by other methods. The possibility of applying the ceramics as the fireproof materials is ensured by high temperatures of synthesis.

Keywords: *high-temperature synthesis, outside the furnace, centrifugal acceleration, solid solutions, spinel, mullite.*

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Preparation of 3D micro components of BST by using a colloidal shaping technique

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Barium strontium titanate (BST) ferroelectric materials have been extensively researched for microwave applications in tunable filters, phase shifters, antennas and so on. However, the consolidation of these structures by using aqueous colloidal shaping techniques is not yet fully explored due to the instability of BST powders when immersed in aqueous media. In fact, it has been reported that when dispersed in water, the constituent alkali-earth ions (Ba^{2+} , Sr^{2+}) are leached out from the powder resulting in a titanium rich surface layer. It was also found that the amount of leached alkali-earth ions increases with decreasing pH. The pH of resulting suspension increases with the extent of leaching and changes the surface chemistry of BST powders, hindering an efficient deflocculating and consequently, the preparation of high concentrated suspensions.

In the present work, a $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ solid solution (BST) was prepared by conventional solid state reaction from BaCO_3 , SrCO_3 and TiO_2 as raw materials. In order to characterize the powder, structural parameters, crystallinity and bulk densities were determined. Aqueous suspensions of BST powder with 50 vol.% solids loading were prepared in the presence of a suitable surface active agent to protect the surface of the particles against hydrolysis. Surface-treated BST powder was found to be water-resistant for several days even in presence of dispersant. Using this suspension an innovative colloidal approach to obtain 3D micro components is disclosed that involves the use of an aqueous soluble resin and hardener to consolidate the structures inside the non-porous moulds (made by silicone). Components less than 1 mm length were casted and easily de-moulded which is a notable advance in the micro components preparation than can prospect high progresses in MEMS in near future.

Preparation of α -alumina nanoparticles with various shapes via hydrothermal phase transformation under supercritical water conditions

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Alumina (Al_2O_3) fine particles are widely used as industrial materials including fillers for metal or plastics, paints, polisher, cosmetics and electric substrates, due to its high hardness, chemical stability, and high thermal conductivity. The performance of those industrial products is closely related to the particle size or shape of the used alumina particles, and thus a new synthetic method to control size, shape, and crystal structure of the aluminum oxide is desired for improvement of the performance. Hydrothermal phase transformation using various aluminum compounds such as oxide, hydroxide, and salt as a starting material, is known as one of the synthetic methods for producing alumina fine particles; however, the size and shape of the starting aluminum compounds have been little mentioned, although they strongly affect the size and shape of the final product. In this study, we investigated the influence of the shape, size and crystal structure of the starting aluminum compounds on those of the product, and newly succeeded in the production of rod-like α - Al_2O_3 nanoparticles from fibrous boehmite nanoparticles.

Starting materials used in this study were amorphous aluminum hydroxide ($\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$), gibbsite ($\text{Al}(\text{OH})_3$), bayerite ($\text{Al}(\text{OH})_3$), and fibrous and pillar-like boehmite ($\text{AlO}(\text{OH})$) sols prepared by sol-gel method using aluminum isopropoxide. Experiments were conducted using a batch-type reactor with 10 cm^3 in volume. The treatment temperature was in the ranges of 400 to 500 °C and the pressure was 15 to 40 MPa. The time was 15 minutes to 8 h. Crystal structure of the product was determined by X-ray diffraction method. The size and shape of the product were observed by TEM and SEM.

We examined the effect of the reaction temperature using fibrous $\text{AlO}(\text{OH})$ sols with 5 nm in width and 1400 nm in length and pillar-like $\text{AlO}(\text{H})$ sols. Reaction pressure and time was fixed to 30 MPa and 5 h, respectively. At 400 °C, the product remained crystalline $\text{AlO}(\text{OH})$. At 450 °C, the product was a mixture of $\text{AlO}(\text{OH})$ and a few α - Al_2O_3 . At 500 °C, when the starting material was fibrous $\text{AlO}(\text{OH})$ sol, α - Al_2O_3 was obtained as a single phase. However, when the starting material was pillar-like $\text{AlO}(\text{OH})$ sols, the product was a mixture of metastable tohdite ($5\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and α - Al_2O_3 even at 500 °C. From TEM observation, the α - Al_2O_3 obtained from fibrous $\text{AlO}(\text{OH})$ sols was rod-like particles with ca. 100 nm in diameter and 200 – 300 nm in length. According to literatures [1,2], as α - Al_2O_3 particles which have been obtained so far under nearly same conditions are plate-like or cubic in shape and relatively large in size, rod-like α - Al_2O_3 fine particles are new. Although a detailed mechanism is unknown, it is considered that the reason why we could obtain fine and rod-like α - Al_2O_3 particles compared with the literatures is derived from the high reactivity of the starting fibrous $\text{AlO}(\text{OH})$ sols.

We also examined the effects of the crystal structure of the starting materials. From amorphous $\text{Al}(\text{OH})_3$ and gibbsite, plate-like tohdite particles with 1 micron meter in diameter were obtained. While, bayerite transformed to plate-like α - Al_2O_3 fine particles with ca. 100 nm in diameter. It is concluded that under hydrothermal and supercritical water conditions, the shape and crystal structure of α - Al_2O_3 fine particles can be controlled by selecting the starting compound of alumina.

Keywords: α - Al_2O_3 , nanoparticle, boehmite, phase transformation, supercritical water ,

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Penetration of carbon into lead zirconate-titanate during sintering by SPS and their dielectric properties

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Bulges were observed on a surface of some of sintered bodies of Pb(Zr,Ti)O₃ (PZT) by SPS, which were heat-treated at 1200°C. Some of the sintered bodies were cracked. Such phenomena were attributed by an existence of carbon in the sintered bodies. Carbon penetrated into the sample during sintering by SPS. The source of the carbon was a carbon paper between sample and graphite die. Penetration phenomena of carbon into a sintered body of PZT during SPS were studied. When starting powder was calcined at 1200°C and pulverized by a “Nanomizer” or by ball-milling, bulges were significant. On the contrary, when the starting powder was calcined at 800°C and ground with pestle and mortar, no bulges were observed. Analysis of the carbon content disclosed that the carbon penetration is high in the sintered bodies of powders pulverized by the “Nanomizer” or by ball-milling. It was revealed that carbon tends to penetrate as the particle size of the starting powder decreases. Dielectric constant of PZT sintered by SPS was low despite its high sintered density. Heat-treatment of the SPS-sintered body was very effective for the improvement of the dielectric property, as long as the carbon penetration affected little.

Keywords: *PZT, SPS, sintering, carbon, nanomizer, ball-milling, bulge, dielectric constant, heat-treatment,*

Preparation of compositionally graded hollow spherical particles of hydroxyapatite/potassium silicate by spray-drying

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In the spray-drying method, an aqueous solution containing dissolved materials is sprayed inside a furnace so that the materials undergo instant drying to form a powder. The powder thus formed consists of hollow spherical particles. We have previously reported the dissolution of hydroxyapatite (HAp) by blowing CO₂, and currently, we are investigating the preparation of hollow spherical HAp particles by spray-drying a HAp solution. However, the wall thickness and mechanical strength of these particles are very low. We have also reported the preparation of compositionally graded particles by spray-drying a solution containing two different elements^[1]. In the present study, we investigate the preparation and measure the mechanical strength of compositionally graded spherical particles by spray-drying such that the resulting particles consist of HAp particles on the outside and potassium silicate particles on the inside that assist mechanical strength.

A potassium silicate solution was added to a high-concentration HAp solution, and the resulting mixture was spray-dried to obtain hollow spherical particles. The obtained particles were 2–5 μm in size. The wall thickness of the particles without the addition of potassium silicate was approximately 200 nm, and this value was increased to 300 nm by adding potassium silicate. Fig. 1 shows the elemental mapping of the internal structure of HAp/potassium silicate hollow spherical particles obtained using electron probe microanalyzer (EPMA). The cross-sectional EPMA image of the particles indicated that Ca from HAp was distributed on the outer surface and the silica from potassium silicate was distributed in the central region of the spherical particles. The compressive strength of the obtained particles was estimated by measuring the compressive strength of one particle. The compressive strengths of a thin-walled hollow HAp particle and a hollow HAp/potassium silicate particle were approximately 0.6 MPa and 1.2 MPa, respectively.

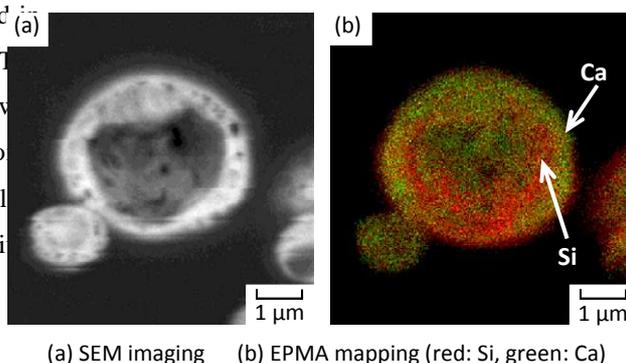


Fig. 1 SEM and EPMA mapping of obtained hollow spherical particles

Keywords: Spray-drying, hydroxyapatite, hollow spherical particles

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Processing of Metal-Ceramic-Precursor Powders for Reaction Bonding and Reactive Sintering of Alumina-Composites

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Reaction bonding and reactive sintering enables processing of low cost advanced metal-ceramic composites. The combination of metals and ceramics either homogeneously distributed offer improved mechanical and tribological properties comparing to single phase ceramics. Due to the reactive sintering metal-ceramic composites with specific properties can be processed, which is exemplified by Cr-Al₂O₃ composites. These reactive synthesis routes are aimed for complete densification by pressureless sintering. The fabrication of these composites is based on powder metallurgical processing techniques, which requires fine grained, homogeneous precursor powders. Metal ceramic powder mixtures (Precursor) are also an important prerequisite to form advanced oxide ceramics like the Reaction-Bonded-Aluminum-Oxide (RBAO). Usually milling of one component, either metal (ductile) or ceramic (brittle) powder, is well described in the literature. Central theme is to demonstrate and understand the process of mechanical alloying between ceramic and metal phases during the milling process. Therefore, wet milling of a powder mixture containing ceramic and metallic particles in non aqueous organic solvents has been investigated. The precursor powders have been wet grinded in an attrition mill. Organic milling liquids with different properties were under examination. The effect of polarity, chemical group affiliation and water content of the solvent on the agglomeration behavior of the particles will be discussed.

Products of hydration in fine grained mixtures MgO - SiO₂.

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The aim of this study was to evaluate the influence of time of ageing on phase evolution of paste from MgO-SiO₂-H₂O phase system. The great interest in this system is related to the Magnesium Silicate Hydrate gels (M-S-H) which are presence in the refractory as a bonding phase.

The paste was composed of fine grained powders of chemical pure magnesium oxide and microsilica in 1:1 molar ratio and water, with water to solid ratio equal 0,5. The obtained mixtures were homogenized by mechanical mixing using the vibratory mixer. After preparation the pastes were ageing during specified time up to 180 days in temperature 20° C.

Phase composition of mixture of MgO and SiO₂ with water was studied by XRD, DTA-TGA and FTIR analysis after different time of ageing. DTA-TGA analysis was performed in the range 20-1000°C, XRD analysis conduct in range 5-90° 2 Theta and the FTIR spectrum was performed in range from 400 to 4000 cm⁻¹.

The analysis revealed that product of reaction in mixture of MgO, SiO₂ and water was a poorly crystalline layer magnesium silicate, probably poorly ordered sepiolite.

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Radiation Curable Coatings for Flame Retardant Polyester Fabric Finishing

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Textile finishing is an important process in the textile industry to obtain particular properties of finished fabrics such as wrinkle resistance, water repellent, flame retardant finishing. Coating is a chemical finishing process producing a finish uniformly distributed throughout the textile material. Ultraviolet curable coating is one of the most widely used in coating industries to change a liquid coating film into a solid film. Due to no heat is required in curing and there is no solvent involved, ultraviolet curing process provides high productivity, energy saving and environmentally friendly process.

In this research, flame-retardant functional UV curable coating formula was prepared and used in polyester fabric finishing application. Physical properties and flame-retardant properties of finished polyester fabric were investigated relative to unfinished polyester. It was found that the coated fabric provided good flame retardant property as the amount of phosphoric contents increased.

Keywords: *flame-retardant, ultraviolet curing, polyester fabric finishing*

Scientific and Technological Aspects of Obtaining Ultradispersed and Mesoporous Powders of Metal Oxides, Metal Silicates and Composites by Wet and Combined Methods

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Ultradispersed and mesoporous metal oxides powders, metal silicates and composites are high demand raw-materials for developing based on them wide range of new materials with improved properties. It's important to develop such technologies, adaptation of which to industrial conditions would to create cost-effective production of new functional materials. Production engineered and environmentally friendly technology was developed for obtaining ultradispersed oxides of metals of II-VIII groups of Periodic Table and composites based on them for the urgent fine-grained ceramics. Modified sol-gel technique with use of N-contained sol stabilizers, template method with use of low-molecular structure directed agents, cryotechnology approaches with use of liquid N₂ (-196°C) and microsuspension method were used for development.

The report presents scientific approaches developed last 5-7 years to technology of:

- fine-grained (0.5-3.0 μm) functional varistor ceramics based on Bi₂O₃ and ZnO with Ni-, Ce-, Y-, Cr- and Co-oxides as additives for small-sized electronic devices;
- bioceramics of fourth generation (fine-grained) for endoprosthesis based on the ultradispersed solid solution powders Ce_xZr_{1-x}O₂ or Y_xCe_yZr_{1-x-y}O₂ (20 nm) and Al₂O₃ (2-4 nm);
- nanostructured and mesoporous catalysts based on metal-silicates and ultradispersed (3-100 nm) metal oxides CeO₂, Co_xO_y, MoO₃, NiO, WO₃ and them composites for petrochemistry and protection of the environment, while for membrane technology.

Compacting and sintering schedules of synthesized ultra dispersed powders were developed for obtaining the fine-grained ceramics with improved properties.

Keywords: *modified sol-gel method, cryotechnology, microsuspension, ultradispersed powders, mesoporous materials, fine-grained ceramics, nanocatalysts*

Spontaneous Formation of Micrometer-Scaled Cell-like Patterns on Alkoxide-Derived Silica Films Induced by Bénard-Marangoni Convection

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Sol-gel coating processes are widely used as the methods for preparing metal oxide films, where micrometer-scaled patterns such as unevenness in thickness or ridges are formed on the surface of the films under certain conditions [1]. Cell-like Bénard-Marangoni convection occurring in the coating layer during solvent evaporation is known as one of the important factors for the pattern formation on sol-gel films [2-3]. Such spontaneous pattern formation on sol-gel films induced by Bénard-Marangoni convection is regarded as a self-organization process, and the surface structure thus obtained holds great promise for the application to photonic devices such as diffraction gratings and microlens arrays. Here, we examined the evolution of surface patterns on alkoxide-derived silica films during solvent evaporation, and evaluated the size and shape of the patterns.

Starting solutions of molar compositions, $\text{Si}(\text{OCH}_3)_4$: H_2O : HNO_3 : $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$: poly(vinylpyrrolidone) (PVP) = 1 : 2 : 0.01 : 5.77 : 0.7, were prepared at room temperature, and served as coating solutions for dip-coating, where PVP of average viscosity molecular weight of 630,000 was employed and the mole ratio for PVP is monomer equivalent. Silica gel films were deposited on Si(100) substrates by dip-coating where the substrates were withdrawn at 50 cm min^{-1} . The dip-coating was performed in a thermostatic oven at 25–100 °C.

The thickness of the silica films increased from ca. 2.8 μm to ca. 7.0 μm with increasing coating temperature. Smooth surface was found in the silica film prepared at 25 °C. On the other hand, cell-like patterns were formed on the surface of the films prepared at 40–100 °C, where the cells arranged parallel to the withdrawal direction. The center and edge of a cell were depressed and elevated, respectively. The height of cell-like patterns increased from ca. 0.02 μm to ca. 1.2 μm , and the width decreased from ca. 200 μm to ca. 170 μm with increasing coating temperature.

Such surface patterns could be caused by Bénard-Marangoni convection due to the surface tension inhomogeneity in sol layers induced by the solvent evaporation. Here, the increase in the coating temperature activates the convection in the solution layer, which promotes the local surface elevation via solution flow, consequently leading to the formation of cell-like patterns of larger heights. On the other hand, the number of the convections per unit volume increased with increasing coating temperature, resulting in the decrease in the width of the patterns.

Keywords: *Sol-gel process, Self-organization process, Micropatterning, Bénard-Marangoni convection,*

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Synthesis and Application of Plate-like Titanate/Cobalt Blue Composite Pigment

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Multifunctional cosmetic materials have been attracted much attention because of their potential application in new generation cosmetic products. The cosmetics showing various colors, a flickering pearlescent effect and a good use feeling are strongly expected. A cobalt/aluminum mixed metal oxide, cobalt blue (CoAl_2O_4), has been widely used as colorant material. Unfortunately, the comfort of using and covering capability on skin of nanoparticles are generally modest because of their small particle size and strong agglomeration. In contrast, the plate-like microparticles show excellent comfort of using and pearlescent characteristic, but usually possess white color only. Therefore, the synthesis of colored plate-like particles becomes an important subject for the application as cosmetics. In the present research, plate-like titanate/cobalt blue pigment composite was successfully synthesized by mixing cobalt blue (CoAl_2O_4) pigment nanoparticles with plate-like lepidocrocite-type potassium lithium titanate ($\text{K}_{0.8}\text{Li}_{0.27}\text{Ti}_{1.73}\text{O}_4$, PLT) microparticles in water in order to improve the comfort and covering ability when applied on skin as cosmetics. Potassium lithium titanate plate like particles were synthesized by KCl flux method at 1000°C for 5 h using K_2CO_3 , Li_2CO_3 and TiO_2 as starting materials, while CoAl_2O_4 nanoparticles were synthesized by mixing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with the molar ratio of Co : Al 1 : 6 at pH 9 followed by calcination at 1000°C for 1 h. The morphology of the plate-like potassium lithium titanate/ CoAl_2O_4 composite strongly depended on the solution pH. Since in a low pH solution, the surface of potassium lithium titanate was negatively charged, while that of cobalt blue was positively charged, CoAl_2O_4 nanoparticles were homogeneously coated on the surface of potassium lithium titanate by electrostatic attraction force. Potassium lithium titanate/ CoAl_2O_4 composites obtained showed nice feeling, high flickering pearlescent, excellent UV-shielding characteristic and novel blue color, indicating its potential application as extender pigments in new cosmetic products.

Keywords: *Plate-like Titanate; Cobalt Blue; Composite; Multifunctional Cosmetic Material*

Synthesis and Characterization of MgAl₂O₄ Nanopowders by a Reverse Micelle Processing

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MgAl₂O₄ nanoparticles was synthesized by reverse micelle processing the mixed precursor (consisting of Al(NO₃)₃ and Mg(NO₃)₂). The Mg ferrite was prepared by mixing the aqueous solution at a molar ratio of Mg : Al = 1 : 2. XRD pattern show that the crystalline phase of the synthesized particles with heat treatment 500°C for 2h is spinel. The average size and distribution of synthesized powders were in the range of 10-20nm and narrow, respectively. The average size of the synthesized powders increased with increasing water to surfactant molar ratio. The XRD diffraction patterns show that the phase of MgAl₂O₄ was spinel (JCPDS no.22-1012). The synthesized and calcined powders were characterized by thermo gravimetry- differential scanning calorimeter (TG-DSC), X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM). The effect of synthesis parameter, such as the molar ratio of water to surfactant, is discussed.

Keywords: MgAl₂O₄ , Nano Powders, Reverse Micelle Process, Refractory

Synthesis and Properties of CrAlSiN Coatings Using a Hybrid HIPIMS/CMS Technology

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As a variation of high power impulse magnetron sputtering (HIPIMS) technique, HIPIMS+ technology is utilizing Modulated Pulse power Supplies (MPP) as cathode power supplies. By increasing the peak cathode current density within the pulse, one can obtain a high degree of ionization of the sputtered material with low ion energies, while at the same time achieving reasonable deposition rate. The HIPIMS+ technique can be utilized to obtain dense coatings with high hardness and low-level residual stress. These characteristics make the HIPIMS+ technology desirable in synthesizing hard coatings. By combining the conventional magnetron sputtering (CMS), the hybrid HIPIMS+/CMS technique is easily to be used for synthesizing multicomponent hard coatings. Chromium based hard coatings, such as CrN, Cr-Al-N and Cr-Si-N coatings have been widely used as a protective coating owing to their high hardness, low friction coefficient, good corrosion and oxidation resistance under severe environmental conditions. Recently, the quaternary Cr-Al-Si-N coatings were attracting more and more attentions due to their various hybrid functions, such as high hardness and excellent oxidation and wear resistance. In this presentation, we synthesize the CrAlSiN coatings by reactive sputtering Cr and AlSi targets in an Ar/N₂ atmosphere. A HIPIMS power and a conventional pulsed DC power were used as the power supply for Cr and AlSi target, respectively. The chemical composition on the microstructure, mechanical and oxidation properties of the coatings were investigated.

Synthesis of new derivatives of Rhodanine dyes for Dye-Sensitized Solar Cells (DSSCs)

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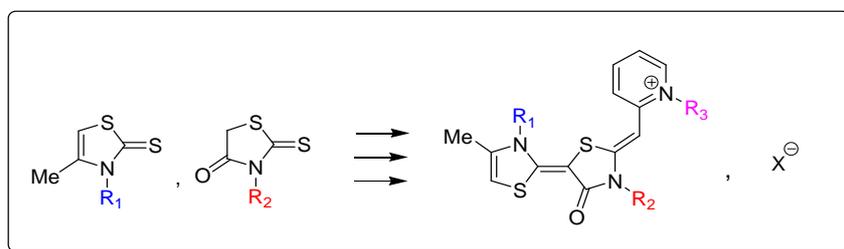
Solar energy is renewable energy par excellence. Environmentally friendly, it has many specific advantages because of the foreseeable depletion of fossil energy resources. The solar cells are currently dominated by silicon and expensive, hence the widespread enthusiasm of researchers interested in the possibility of manufacturing solar cells from plastic materials or organic.

These new cells have the advantage of being simpler and more malleable than those made from a silicon^[1].

Several organic dyes, such as styryl^[2], coumarines^[3], polyenes^[4] and indole derivatives^[5], have been proposed as potential candidates for solar cells.

Rhodanine derivatives, electron acceptors are used in a wide range of organic molecules "Push-Pull" These have applications in optics and more recently non linéaire^[6] are used in the manufacture of DSSCs^[7] and are obtained with a high conversion efficiency compared to other.

We were interested in the synthesis of new chromophores containing the pattern rhodanine, a molecule from the leader aminothiazoline thione as a synthetic strategy developed previously in our laboratory.



Chromophores obtained and intermediate compounds were identified by spectroscopic methods (1H NMR, 13C, IR and mass spectrometry).

Keywords: DSSCs, Rhodanine, Merocyanine, Dye, Photovoltaic cells.

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The role of phosphorus in the archaeometallurgy of iron – investigation of the bloomery technology with the help of laboratory models

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In recent years it has been indicated with archaeometric investigations on mainly medieval knife and sword blades that phosphoric iron with relatively high or in some cases very high phosphorus content (0.5-2w%) was used in the creation of these blades, with decorative purposes or for increasing hardness [1,2,3]. By archaeometric investigations of slag and iron ore samples from the 9-10th century excavated in Somogy county we have found that phosphorus had an important role in the local archaeometallurgy of iron [4]. This cannot be seen in all the archaeological findings of the Carpathian basin, whereas it can be paralleled with other European findings, in Scandinavia, for instance [5]. A question can be raised on how the distribution of phosphorus between the metal and the slag phase depended on the quality and quantity of the bog iron ore, charcoal and air supply?

We have solved the above mentioned archaeometry-related problem with experiments conducted with laboratory models [6] built on the basis of previously conducted smelting experiments [7], which are faithful representations of period smelting processes. These models, which can be investigated by technological parameters, can easily be reproduced. We conducted the experiments in a closed pot (closed model) and in a small shaft furnace (open model) with bog iron ores of different phosphorus content. In the case of the open model experiments we also changed the volumetric flow rate of the air supply. We performed XRF and XRD analyses on the bog iron ore samples used in the experiments, and OM, SEM-EDS and ICP analyses on the extracted slag and iron samples.

On the basis of the material analyses there was a significant difference in the phosphorus distribution between the slag and iron phase in the closed and open model experiments. While in the closed model we got hypereutectoid, phosphorus free iron phase, in the open model the phosphorus content of the hypoeutectoid iron phase was significantly higher. In both models, the basic characteristic of the mine rubbish of the bog iron ore had a considerable effect on the phosphorus content of the iron phase. In the open model, the volumetric flow rate of the air supply also affected the phosphorus distribution. Our exemplary, interdisciplinary experimental project based on modern material analyses and laboratory technology can be used both for solving archaeometallurgical problems and for the investigation of the chemical-metallurgical aspects of modern direct reduction metallurgical processes.

Keywords: *Archaeometallurgy, phosphorous distribution, laboratorial model, direct reduction*

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Session 10.
Organo-Clay Complexes

Removal of Organic Pollutant from Water by The Use Modified Bentonite

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This study investigated the possibility of removing organic pollutants from water by using organo-Bentonite. The organo-bentonites were synthesized by ion exchange reaction using quaternary ammonium or phosphonium organic salts. The resultant organo-bentonite complexes were lyophilized, grounded to 5 μ m and used as test materials. Bromoxynil, is a widely used herbicide was taken as a standard water pollutant in this study because it has been detected in many water samples around the globe. The experimental design of this study based on adsorption/desorption techniques. Bromoxynil concentrations in equilibrium solution were determined by HPLC. Results showed that bromoxynil was adsorbed in organo-Bentonite (Bentonite -NCP, and/or Bentonite-HDTBP) several times higher than in hydrophilic bentonite surfaces. The adsorption of bromoxynil to organo-Bentonite was further enhanced by lowering the pH of the solution, and optimizing the temperature for the adsorption reaction. Desorption of bromoxynil from NCP-, or HDTBP-bentonite was significantly slower than from raw bentonite. Desorption at acidic solution (pH 3) was significantly slower than at solution of pH 5.5 or distilled water. These results indicate the efficacy of organo-bentonite to remove organic pollutants from water, accordingly application of organo-bentonite may be advantageous materials for removing organic pollutants at a large scale.

Keywords: *Bromoxynil, Organo-bentonite, bromoxynil, Adsorption*

Using the resistivity measurements for controlling the effect of lime milk on dispersive soils

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Internal erosion is one of the major reasons for earth structures failures. The presence of dispersive clay at the embankments increase the risk of this phenomenon development inside the dam body because this type of clay arestructurally unstable, easily dispersive when it contacts the water and, thus, highly erodible.

Several studies have been done to stabilize and improve the dispersive nature using chemical products such as: lime, cement, fly ash.... In our research, we have used the milk of lime for the treatment of a dispersive soil. This technique has many advantages, especially for the cost and it is easily executed. At laboratory the erosion tests show that the addition of a small percentage of lime milk decreases the soil sensitivity to the dispersion, and increase its resistance against erosion.

To check the technique validity in situ, we have used the resistivity measurements. This method is well suited for dam monitoring as it is non-destructive and easily adapted for long-term monitoring. For that, an experimental laboratory study was realized, we have prepared many samples with different percentage of lime milk, and resistivity measurements are taken.

Keywords: *Internal erosion, Dispersion, Traitement, Milk of lime, Resistivity, Laboratory.*

Scanning tunneling microscopy study of Fe(CO)₅ and Fe(C₅H₅)₂ adsorption on Si(111)7×7 .

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The adsorption at room temperature of ferrocene and iron pentacarbonyl on Si(111)7×7 have been studied. On Si(111)7×7, the adsorption sites have been identified by means of scanning tunneling microscopy. We propose a ferrocene adsorption model on Si(111)7×7, i.e., a di-sigma bridging by the molecule between an adatom and a restatom site similar to that proposed for the ethylene. For the iron pentacarbonyl, we have found evidence of a dissociative adsorption on nucleophilic sites. At a higher temperature, an exposure to iron pentacarbonyl lead to the growth of good quality iron silicide. Whereas, silicide carbide is formed on exposure to ferrocene. The films obtained can be explained by means of the chemisorption process at room temperature.

Keywords: *STM, Si(111)7×7, adsorption, iron pentacarbonyl, ferrocene.*

Session 11.

Phase Diagram as a Tool of Materials Science

Approximate Calculation of the MgO Rich Corner of the MgO-Al₂O₃-CaO-SiO₂ Phase Diagram by ESTPHAD Method

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The ESTPHAD (Estimation of Phase Diagrams) method is based on thermodynamic principles, and the algorithm is suited for approximate calculation of transformation curves and surfaces of phase diagram. The ESTPHAD method uses measured temperature and concentration data as the most types of phase diagram calculation method. In this work we have done calculations in the MgO rich corner of the MgO-SiO₂-Al₂O₃-CaO quaternary system. The ESTPHAD method has a hierarchical structure, so first of all we worked in binary MgO-SiO₂, MgO-CaO and MgO-Al₂O₃ systems, and later we cared the MgO-Al₂O₃-CaO, MgO-Al₂O₃-SiO₂ and MgO-CaO-SiO₂ ternary systems by using both of the binary calculated data and ternary measured data from literature. Finally, we have approximated the liquidus temperature data in the MgO-Al₂O₃-SiO₂-CaO quaternary system.

Complex sulfides, as a new class of advanced synthetic materials

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The progress of science and technology requires a constant search for new materials. Important task of modern chemistry is the synthesis of new, promising inorganic compounds on the basis of which it is possible further development of materials science. Complex sulfides s-, d- and f-elements exhibit a wide range of properties. On the basis of complex sulfides optical, thermoelectric, strain gage material were established.

The structure of simple and complex sulfides should be considered at different levels of structure (mid-, micro-, nano-), each of which formed the elements of the structure and accordingly determined the quantitative values of properties in complex sulfides are realized the main types of chemical bonds, metallic, covalent, ionic. The metallic bond is present in the phases $\text{Ln}^{\text{III}}\text{S}$, in which the atoms of rare-earth elements are not associated with the sulfur atom 5d- or 4f- electron. Delocalisation of 5d- 4f- electrons leads to the appearance of characteristic properties of the phases for the metals. Minor differences in the electronegativities of copper and sulfur determine the type of covalent chemical bonds in the compound Cu_2S and semiconducting properties of the phase. The manifestation of the semiconducting properties of the compounds and are expected to type $\text{A}^{\text{II}}\text{LnCuS}_3$. Growth of differences in electronegativity of metals and sulfur compounds in the $\text{A}^{\text{II}}\text{S}$, Ln_2S_3 increases ionic component of chemical bonding. On electrical properties of complex sulfides, compounds Ln_2S_3 are medium and wide-gap semiconductors.

The mechanical action on thin film materials, located on the borders of the micro- and meso-levels, leads to a flip of electrons from impurity levels to the conduction band. Then the electrical conductivity of the film is linearly proportional to the mechanical load, which allows the use of film as the sensing element of pressure sensors and effort.

At the meso-level are formed crystallite and the grain structure of the phases, a screw dislocation. State of the surface sulfide is crucial to contact phenomena, such as contacts in the thermoelectric power. The change in surface topography processes was established by force microscopy. Spikes, sharp protrusions are formed during the growth of grains during annealing. Commodity products are sulfides powders, products, samples cut from molded, compressed tablets and cubes. Understanding the processes of defect formation can determine the conditions for obtaining and using products that significantly reduces the percentage of substandard products.

Keywords: *sulfide compounds, structure, surface effects*

Crystallization paths in SiO₂-Al₂O₃-CaO system as a genotype of silicate materials

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Computer model of phase diagram permits to analyze the crystallization stages for any composition. The system A-B-C with an incongruently melting compound R=AC has 5 concentration fields (3 one- and 2 zero-dimensional) without a unique crystallization scheme and a unique microstructure set [1, 2]. They can be considered as belonged the neighboring concentration fields with one-more dimension. Two more fields with the reaction $L+A(Q)=B(Q)+R(Q)$ - two-dimensional field and adjoining fragment of liquidus curve - have the identical microstructure, but differ in the phase reactions. The reactions $L(1)=A(1)$, $L(e)=A(e)+B(e)$, $L(Q)+A(1,e)=B(Q)+R(Q)$, $L(e)=B(e)+R(e)$, $L(E)=B(E)+C(E)+R(E)$ with the deposition of microstructure elements B(e), B(Q), R(Q), B(e), R(e), B(E), C(E), R(E) occur in two dimensional field between a point Q and a quasibinary system B-R. As melt in this field is in excess in relation to the reaction $L+A(Q)=B(Q)+R(Q)$, then the crystals A(1) and A(e) are absent. One-dimensional field on the border of this two-dimensional field has the same microstructure, but differs by the reaction $L(1)=A(1)$ missing, because it is a part of monovariant liquidus curve. It is known also that there is a two-dimensional field, bordered by A-B system, which is divided into three fragments as the result of competition of crystals A(e), A(1) with different dispersity in the reaction $L+A(Q)=B(Q)+R(Q)$ [3].

The analysis of crystallization paths in the system with incongruently melting ternary compound ABC was characterized as "rather complicated" [4, P. 177]. We have realized the computer model of this phase diagram and determined 65 concentration fields (11 zero-, 32 one- and 22 two-dimensional types). From them 13 fields haven't the individual crystallization schema and microstructure sets, but 5 fields differ only by phase reactions sets.

System CaO-Al₂O₃-SiO₂ includes 117 two-, 163 one- and 45 zero-dimensional fields. Its T-x-y diagram is characterized by 16 invariant transformations (9 – quasiperitectic, 6 – eutectic and 1 - with the participation of two SiO₂ allotropies) and includes 33 two-phase and 46 three-phase regions. Any crystallization stage also can be illustrated by the material balances: vertical - for the given composition, and horizontal – as isothermal states of isopleth.

Keywords: *phase diagram, system CaO-Al₂O₃-SiO₂, 3D model, crystallization path, microstructure*

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Development of Advanced Materials Based on Phase Diagrams

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Recent progress in the development of advanced materials based on the study of phase diagrams and microstructural control is presented. Thermodynamic databases on the Fe-S based system, Cu-based alloys and Co-based superalloys have been constructed. By utilizing these databases and information on phase diagrams, the following advanced materials have been developed.

1. Pb-free machinable low alloy steels using chromium sulphide.
2. Pb-free machinable stainless steels using titanium carbosulphide.
3. Ingrown nail correcting device using Cu-Al-Mn based shape memory alloy.
4. Cu-Ni-Al based alloys with high strength and high electronic conductivity strengthened by γ' (Ni_3Al) phase.
5. FSW (Friction Stir Welding) tool using Co-based superalloy strengthened by γ' ($\text{Co}_3(\text{Al}, \text{W})$) phase.
 - 1.
 2. The alloy design and practical application of these materials focussing on the use of phase diagrams will be presented.

Keywords: *Thermodynamic database, Practical applications, Lead-free machinable steels, Cu-Al-Mn-base shape memory alloys, Co-base superalloys*

New Phase Regions of Ir-Ru-Ti System with Eutectic-Peritectic Transformations

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Reaction $L \rightarrow \epsilon + Ru$ ($\epsilon = TiIr_3$) change for $L + \epsilon \rightarrow Ru$ has been known in A-B-C=Ti-Ir-Ru system, where (http://www.springermaterials.com/docs/info/10916070_53.html) $R1 = TiIr = \delta = R$, $R2 = TiRu = \delta = R$ ($R1$ and $R2$ form solid solution), $R3 = TiIr_3 = \epsilon$, $R4 = Ti_3Ir = \gamma$. Computer model of T-x-y diagram gives additional information (Fig. 1-2) about this and similar processes in the system. Regions with liquid phase $L + \gamma + \delta$ and $L + Ti + \delta$ have surfaces of 2-phase reaction in temperature intervals 1497-1465° and 1552-1465°. Subsolidus region $Ir + Ru + \epsilon$ is divided by 3 surfaces of 2-phase reaction into 4 fragments. Region $Ru + \delta + \epsilon$ has 3 surfaces of 2-phase reaction ($\Delta m_{Ru} = 0$, $\Delta m_{\delta} = 0$ and $\Delta m_{\epsilon} = 0$), and they divide it into 6 fragments. So, eutectoid reactions are fulfilled in 3 of them and peritectoid ones are carried out between them. Reaction $\gamma + Ti \rightarrow \delta$ is changed for $\gamma \rightarrow Ti + \delta$.

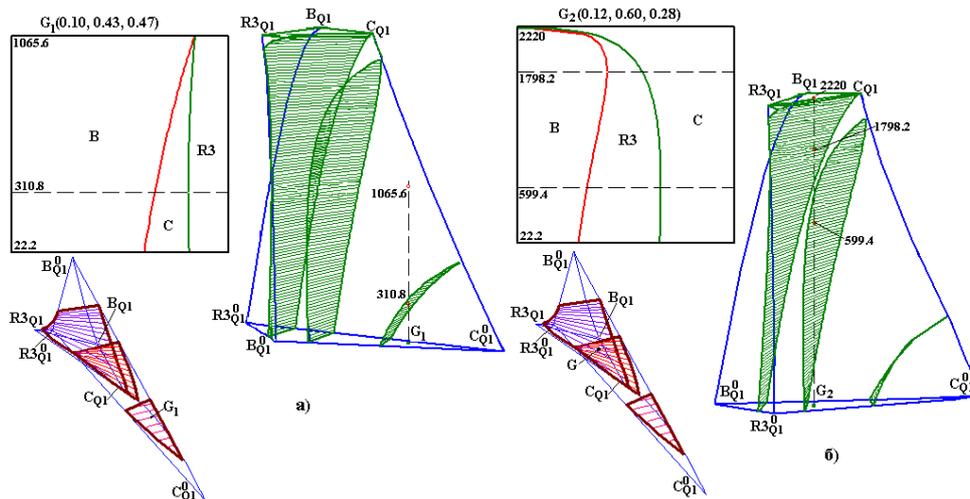


Figure 1. Two-phase reaction surfaces with reaction type change: $B \rightarrow C + R3$ ($Ir \rightarrow Ru + \epsilon$) for $B + R3 \rightarrow C$ (alloy G_1 , $\Delta m_{R3} = 0$) (a), $C \rightarrow B + R3$ for $B + C \rightarrow R3$ and then for $B \rightarrow C + R3$ (alloy G_2 , $\Delta m_B = 0$ & $\Delta m_C = 0$) (b)

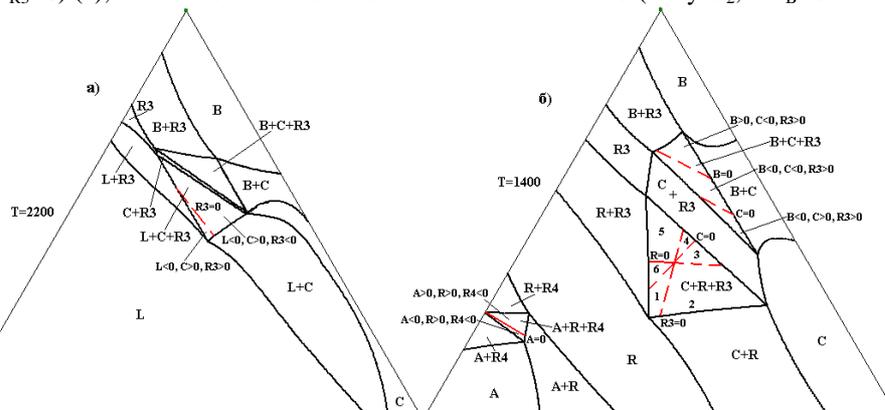


Figure 2. Isotherms 2200 (a) and 1400 (b) with the fragments of phase region $C + R + R3$: 1 - $C > 0, R < 0, R3 > 0$; 2 - $C > 0, R < 0, R3 < 0$; 3 - $C > 0, R > 0, R3 < 0$; 4 - $C < 0, R > 0, R3 < 0$; 5 - $C < 0, R > 0, R3 > 0$; 6 - $C < 0, R < 0, R3 > 0$

Keywords: transformation in 3-phase region, phase diagram computer model, Ti-Ir-Ru

Magnetic Nano-spheres from a Non-magnetic Material: a Possible Explanation

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It is known that if a sphere is constructed from a non-magnetic metal (for example Au), and the size is decreased to nanoscale values, the material can become ferromagnetic [1,2]. For this effect we provide below a possible explanation, which requires only Coulomb repulsion between itinerant carriers and related quantum mechanical effects.

We analyze for this reason a two dimensional $L \times L$ square lattice at arbitrary but finite L size with periodic boundary conditions in both directions, and on-site Coulomb repulsions on each site. This Hubbard system is solved exactly for the ground state in restricted regions of the parameter space in the low concentration limit. The solution procedure (see [3,4] for details) based on positive semidefinite operator properties, first transforms in exact terms the Hamiltonian \hat{H} of the system in a positive semidefinite form $\hat{H} = \hat{P} + C$, where \hat{P} is a positive semidefinite operator while C is a constant scalar. Since the spectrum of \hat{P} is bounded from below by the zero minimum eigenvalue, in the second step we deduce the exact ground state $|\Psi_g\rangle$ by constructing the most general wave vector which satisfies the relation $\hat{P}|\Psi_g\rangle = 0$. The ground state energy becomes $E_g = C$. The ground state is ferromagnetic for number of electrons $N \in (L, 2L)$ and has the form $|\Psi_g\rangle = \prod_i \hat{B}_{i,\sigma}^\dagger |0\rangle$, where $|0\rangle$ is the bare vacuum state, and $\hat{B}_{i,\sigma}^\dagger$ are extended operators with specific vortex structure, being built up from linear combinations of creation Fermi operators with fixed spin projection σ acting on different sites of the system. The parameter space region where the solution emerges is not severely restricted, and flat bands in the bare band structure are not present.

The periodic boundary conditions in both directions lead to a closed surface on a grain which approximates a metallic sphere with mobile carriers only on its surface. \hat{H} has only on-site interaction terms and fixed hopping integrals, hence is not sensitive to folding. If the sphere is macroscopic ($L \sim 10^{26}$), the concentration range ($\rho = L/L^2 \sim 1/L$) where the effect emerges $\rho = 10^{-26} \sim 0$ is practically missing. But for nanoscale, for example $L=10$, leading to $\rho = 1/10$, the effect is observable, and the nanograin behaves as ferromagnetic object. We also analyze in details the conditions for which this effect emerges.

Keywords: ferromagnetism, ferromagnetic nanoparticles, 2D Hubbard model, exact ground states

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Magnetic Measurement of Phase Transformations in Lean Duplex Stainless Steel

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In the present work the microstructure and the strain induced phase transformation of the V2101Mn type lean duplex stainless steel was investigated. The phase transformation of the metastable austenite (γ) to the thermodynamically more stable α' -martensite due to cold rolling was studied. Samples were cold rolled to 20%, 40%, 60% and 80% thickness reduction. The phase identification was done by optical and scanning electron microscope. Vickers hardness tests were also performed on each specimen.

The magnetization curves were measured by a permeameter-type magnetic property analyzer. The magnetic measurements were carried out by using sinusoidal excitation at a frequency of 5 Hz. The applied maximal excitation field strength was 1500 A/m. The series of symmetrical minor hysteresis loops and the saturation loop were measured.

The multiphase hyperbolic model (MHM) was applied for data evaluation of the measured results. The MHM model presents a phenomenological mathematical description of magnetic, sigmoid shaped hysteresis loops and normal magnetization curves in closed mathematical form. This model facilitates the linear superposition of the individual sigmoid loops and indeed provides the way to separate the simple phases and/or the different parallel magnetic processes acting in an alloy during magnetization.

It was proved that the magnetically different magnetic phases of the LDS steel (i.e. ferrite, martensite) can be separated and their individual magnetization curves can be determined. The application of model based data evaluation technique (MBDA) seems to be a promising tool in data evaluation of magnetic measurements.

Keywords: *stainless steel, phase transformation, magnetic testing*

MnS – Tm₂S₃ Phase Diagram

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According to French researchers in the system MnS – Tm₂S₃ form two complex sulphides of compositions MnTm₂S₄ (cubic structure, type MgAl₂O₄) and MnTm₄S₇ (monoclinic, type FeY₄S₇). It is known that the compound MnTm₂S₄ is a dimorphic. We have not found any data on a MnS – Tm₂S₃ phase diagram in the literature. The thermal stability ranges and character of the melting of complex sulfides are not known.

MnS – Tm₂S₃ system are formed two complex sulphide MnTm₂S₄ and MnTm₄S₇ (Fig. 1). The compound MnTm₂S₄ dimorphic: cooled from melt and stable at high temperature β -MnTm₂S₄. Highly temperature modification at annealing at 1170 K for 3 months is formed modification α -MnTm₂S₄. The thermal effect at 1250 K of the transition α -MnTm₂S₄ \leftrightarrow β -MnTm₂S₄ were determined by differential scanning calorimetry (DSC) for samples annealed at 1170 K and containing 48-55 mol. % Tm₂S₃. Microhardness for sample of β -MnTm₂S₄ is 3960 MPa and determined by durometric analysis (DMA). The β -MnTm₂S₄ melting temperature is 1845 K. The presence of a hollow maximum on the liquidus curve for sample containing 48-55 mol. % Tm₂S₃ and position of the solidus line indicate congruently melting compounds β -MnTm₂S₄. Microhardness of low-temperature modification α -MnTm₂S₄ is 3520 MPa. As shown by X-ray powder diffractoin (XRD) the β -MnTm₂S₄ is a cubic structure (structure type MgAl₂O₄), α -MnTm₂S₄ is a orthorhombic structure (type FeY₄S₇). The unit cell parameter a of β -MnTm₂S₄ $a = 1.0950$ nm and parameters a, b, c of α -MnTm₂S₄ $a = 1.243$ nm, $b = 1.250$ nm, $c = 0.364$ nm are determined by software package PDWin 4.0 and Powder 2.0.

The complex sulphide MnTm₄S₇ is formed at a ratio 2 Tm₂S₃ : 1 MnS. X-ray diffractoin diagrams of the sample 66.6 (6) mol. % Tm₂S₃, cooled from the melt, annealed at 1670 K and 1170 K does not contain reflections starting sulphides Tm₂S₃ and MnS. On the x-ray diffractoin patterns are present reflections characted only monoclinic structure complex sulphide MnTm₄S₇. The unit cell parameters for sample MnTm₄S₇ is $a = 1.252$ nm, $b = 0.373$ nm, $c = 1.134$ nm, $\beta = 105.27^\circ$ calculated by PDWin 4.0 and Powder 2.0. The temperature of congruent melting of the compound MnTm₄S₇ fixed at 1855 K. The microhardness MnTm₄S₇ is 3675 MPa.

On the basis of the initial sulfides Tm₂S₃ and MnS are formed a limited range of the solid solutions. Composition versus unit cell parameter diagrams give a value of 16 mol. % Tm₂S₃ at 1670 K and 11 mol. % Tm₂S₃ at 1170 K for boundary compositions of the solid solutions on the MnS-based. Solubility on the basis of the monoclinic structure of δ -Tm₂S₃ are 94 mol. % Tm₂S₃ at 1670 K, 96 mol. % Tm₂S₃ at 1170 K. The boundary solubility determined by fracture of the dependence of "unit cell parameter of the cubic structure – compositions of the samples" and confirmed of the dependence "compositions of the samples – microhardness."

Two-phase areas: MnS and MnTm₂S₄, MnTm₂S₄ and MnTm₄S₇, MnTm₄S₇ and Tm₂S₃ are eutectic type. The coordinates of the eutectic points determined by vision polythermal analysis (VPTA) and microstructure examination (MSA).

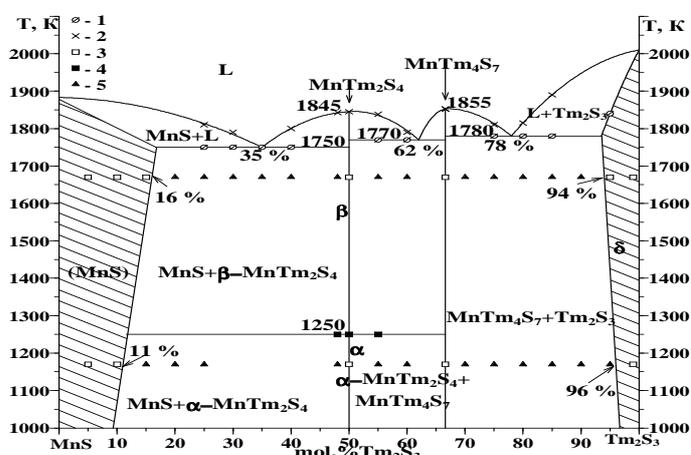


Fig.1. Phase diagram of the system MnS – Tm₂S₃. VPTA data: 1 – the beginning of melting, melting of eutectic crystals, 2 – complete melting; DSC data: 4 – polymorphic transition; the state of the samples as determined by MSA and XRD: 3 – homogeneous samples, 5 – comprising two phase.

Keywords: phase diagram, sulphides, rare-earth elements, eutectic, solid solution.

Phase Equilibria in the Na,K//SO₄,CO₃,HCO₃-H₂O System at 50°C

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In this paper we consider the results of the prediction of phase equilibria in the quinary Na, K//SO₄, CO₃, HCO₃-H₂O system at 50°C by means of translation method. The translation method originates from the compatibility principle of structural elements of *n*-component subsystems and global (*n*+1)-component system in a single diagram [1]. It allows us to predict the phase equilibria in the global (*n*+1)-component system on the basis of data on phase equilibria in *n*-component subsystems, and using the results of this prediction taking into account the Gibbs phase rule [2] enables us to construct a closed phase diagram for global (*n*+1)-component system which is under consideration. Thus constructed closed phase diagram of the multicomponent system can more accurately identify its equilibrium phases, significantly reducing time and cost of its experimental study. The prediction of phase equilibria and construction of phase diagrams for multicomponent systems by means of the translation method are comprehensively considered in literature [3-5]. This method has earlier been employed to study the phase equilibria at 0 and 25°C in the title system [6, 7].

32 divariant fields, 36 univariant curves, and 13 invariant points are determined in the system. The first closed phase diagram (phase complex) of the title system is constructed.

Keywords: *multicomponent phase equilibria; translation method; compatibility principle; Gibb's phase rule*

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Phase stabilities and phase diagram in ternaries systems based on titanium : Experimental investigations, ab initio calculations and Calphad mode ling

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Through a strong collaboration, during the past twelve years, we have studied the phase stabilities and phase equilibria in ternary systems based on titanium. Titanium alloys are very important materials for modern developments in medicine and aerospace applications. Following aluminium and magnesium alloys, they are materials that can participate in the sustainable development of the society by increasing the life -time of materials and saving resources. This is due to a good combination of chemical, physical and mechanical properties. In such systems, we try to understand the phase stabilities when titanium is alloyed with elements possessing different properties. The particularity of these alloys is based on :

a - the relationship of α/β titanium solid -solutions and the intermetallic compounds with $D0_{19}$, $B8_2$, $D8_8$ or $D8_m$ structures.

b - In some systems, the existence of many different ternary compounds has been emphasized.

c - A good knowledge of the phase stabilities allows to understand the behaviour of alloys and systems.

The results obtained in four systems will be presented and a special mention will be done on the Ni -Sn-Ti systems.

1 - Experimental. In those systems t he phase equilibria have been studied experimentally within a lot of samples in those systems in the tin poor part. We have studied the microstructures and the crystal structures below the solidus temperature and in selected isothermal sections. In this study, we have evidenced ternary intermetallic phases (ordered or disordered).

2 - Ab initio. We have used the DFT based VASP package making use of the PAW technique within the generalized gradient approximation and obtained the enthalpies of formation at $T=0K$ of all the binary and ternary compounds. The stability of the ternary phases were modeled and a description of the stabilities of ternary phase has been obtained.

3 - Calphad modeling. With the information obtained from the experimental determinations and the ab-initio calculations, we performed a Calphad modeling of the system. We determined the invariant reactions in the whole system s. The results show a good compatibility between the experimental and theoretical approaches and the work is presently in progress.

Scope of alloying compound CuSc_3S_5 by Lutetium

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Interest, in simple shows by many researchers and complex sulfides, due to the considerable variety of its properties (metals, semiconductors, insulators, superconductors) and their presence on homogeneity range. Quantitative values of material properties determine the possibility of their practical use. Changes in the composition cause a change in properties of the phases that can specifically control the properties of materials. Employees of Institute of inorganic and physics chemistry of Science Academy in Baku, in the 70s of last century studied mainly the electrical properties of compounds formed in the system $\text{Cu}_2\text{S}-\text{Ln}_2\text{S}_3$ ($\text{Ln} = \text{La}-\text{Lu}, \text{Sc}$). The phases are semiconducting type of conductivity on temperature. Possible applications of copper-lanthanide sulfides associated with the creation of a thermoelectric element of the p- Cu_2S branch, $\text{Ln}_2\text{S}_{3-x}$ n-branch, high-temperature resistors.

In experimentally constructed phase diagram of the $\text{Sc}_2\text{S}_3-\text{Cu}_2\text{S}$ established the formation of two complex sulfide melting in peritectic reaction: CuScS_2 hexagonal crystal system, space group P3m1 with unit cell parameters: $a = 0.3734$, $c = 0.6102$ nm, $T_m = 1635$, K $\Delta H_m = 3470$ kJ/mol; CuSc_3S_5 cubic system, space group. Fd3m, with unit cell parameters $a = 1.0481$ nm, $T_m = 1835$ K. The compound melts CuSc_3S_5 by a peritectic reaction:



The close values of ionic radii and electronegativity values of scandium and lutetium, suggest a close nature of phase equilibria. Data on the early experimental phase diagrams of systems built by the third group of $\text{Cu}_2\text{S}-\text{Ln}_2\text{S}_3$ ($\text{Ln} = \text{Dy}-\text{Er}$) mathematically approximated by a specialized program for REE EdstateT end of the series. In mathematically the predicted phase diagram of the system $\text{Cu}_2\text{S}-\text{Lu}_2\text{S}_3$ predicted the formation of two compounds and CuLuS_2 Cu_3LuS_3 , characterized by polymorphism and melting congruently. High-temperature modifications relate to the phases bertolid type. The maximum melting point for compound Cu_3LuS_3 falls on the composition of 40mol% Lu_2S_3 (1670 K), the connection CuLuS_2 - 62mol% Lu_2S_3 (1880 K).

As a priority, we plan to investigate the possibility of doping of complex compounds CuSc_3S_5 lutetium, for a given thermoelectric materials. Close view of the atomic characteristics of scandium and lutetium there is the possibility of substitution of scandium lutetium atoms in the compound CuSc_3S_5 . As a result, the connection of $\text{CuSc}_{3-x}\text{Lu}_x\text{S}_5$ should be observed thermoelectric properties suitable for practical use.

Keywords: *sulfide compounds, structure, surface effects*

The binary systems FeS – Ln₂S₃ (Ln = Tm, Yb, Lu)

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Phase diagrams of systems FeS – Ln₂S₃ (Ln = Tm, Yb) are the same type and characterized by the formation of two complex sulphide Fe₄Ln₂S₇ and FeLn₄S₇.

FeS – Yb₂S₃ system are formed two complex sulphides Fe₄Yb₂S₇ (4 FeS : 1 Yb₂S₃) and FeYb₄S₇ (1 FeS : 2 Yb₂S₃), which melt congruently at 1620 K and 1880 K, respectively. Between phases of FeS and Fe₄Yb₂S₇ is formed peritectic. The compound Fe₄Yb₂S₇ first obtained. X-ray powder diffractoin (XRD) data for the phase Fe₄Yb₂S₇ indexed on the basis of data for the phase Fe₄Sc₂S₇ in the spinel structure with cubic unit cell parameter $a = 1.0660$ nm is determined by software package PDWin 4.0 and Powder 2.0. The microhardness of the phase Fe₄Yb₂S₇ is 4000 MPa. Complex sulphide FeYb₄S₇ according to X-ray diffraction is monoclinic structure with unit cell parameters $a = 1.242$ nm, $b = 0.366$ nm, $c = 1.127$ nm, $\beta = 105.1^\circ$. Microhardness of the crystals phase FeYb₄S₇ is 5000 MPa. The limited solid solutions based on the phases Fe₄Yb₂S₇, FeYb₄S₇, Yb₂S₃ not formed. The coordinates of eutectic points: between the phases and Fe₄Yb₂S₇ FeYb₄S₇ - 33 mol. % Yb₂S₃, 1550 K; between FeYb₄S₇ and Yb₂S₃ 78 mol. % Yb₂S₃, 1800 K. Peritectic between phases FeS and Fe₄Yb₂S₇ has coordinates 2 mol. % Yb₂S₃, 1480 K.

FeS – Tm₂S₃ system are formed two complex sulphides Fe₄Tm₂S₇ and FeTm₄S₇. The phase Fe₄Tm₂S₇ has first obtained and crystallized at MgAl₂O₄ (spinel) structure with unit cell parameter $a = 1.0712$ nm, the microhardness of crystals phase 3800 MPa, melting congruently at 1580 K. The compound FeTm₄S₇ has a monoclinic structure with unit cell parameters $a = 1.247$ nm, $b = 0.369$ nm, $c = 1.129$ nm, $\beta = 105.5^\circ$, microhardness 4900 MPa, temperature of congruent melting 1920 K. Between phases Fe₄Tm₂S₇ and FeTm₄S₇, FeTm₄S₇ and Tm₂S₃ are formed eutectic; FeS and Fe₄Tm₂S₇ are formed peritectic at 1475 K.

The phase diagram of FeS – Lu₂S₃ is a distinctive type of diagram from the previous systems. In the system are formed two complex sulphides Fe₄Lu₂S₇ and FeLu₂S₄. Complex sulphide Fe₄Lu₂S₇ first obtained (Fig. 1.). This compound has a spinel type structure with unit cell parameter $a = 1.0566$ nm, the microhardness is 4100 MPa. The limited area of solid solution Fe₄Lu₂S₇-based is formed. The temperature of congruent melting phase Fe₄Lu₂S₇ at 1670 K. X-ray powder diffractoin data of complex sulphide FeLu₂S₄ identified in a cubic spinel structure type with unit cell parameter $a = 1.0709$ nm, the microhardness is 4000 MPa, the temperature of congruent melting point at 1820 K. On the FeLu₂S₄-based is formed a solid solution of one-sided in the direction of the phase Lu₂S₃. The sample containing 53 mol. % Lu₂S₃ (annealing 1070 K) homogeneous (parameter increase to $a = 1.072$ nm). The coordinates of the peritectic in the subsystem FeS - Fe₄Lu₂S₇ is 2 mol. % Lu₂S₃, the temperature 1175 K. The eutectic between the phases Fe₄Lu₂S₇ and FeLu₂S₄ formed at 27 mol. % Lu₂S₃, 1600 K; between the phases FeLu₂S₄ and Lu₂S₃ at 63 mol. % Lu₂S₃, 1730 K.

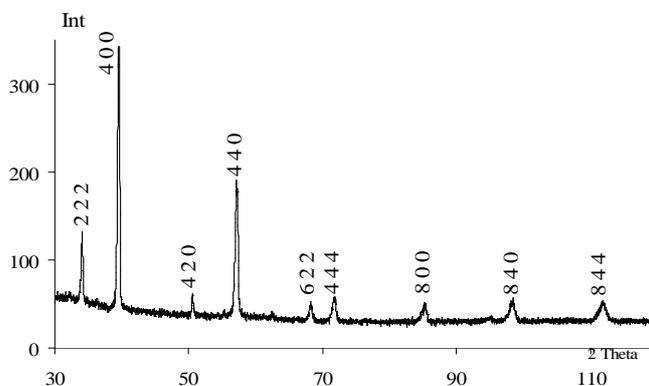


Fig. 1. X-ray diffraction pattern of a complex sulphide Fe₄Lu₂S₇. Parameters of the experiment: CoK α radiation, Fe-filtered.

Keywords: phase diagram, sulphides, rare-earth elements, FeS

The Method For Investigating The Structurization Of Water-Organic Mixtures

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The spectral and time characteristics of the spatial-temporal structures luminescing when exposed to UV radiation in aqueous alcohol solutions of anthraquinone are investigated experimentally depending on the volume content of alcohol in a mixture. It is shown that the microheterogeneous structure of aqueous alcohol solutions considerably influences the behavior of the dissipative structures formed.

The effect of the appearance of self-organization in open systems – the formation of the so-called "dissipative" structures – has found widespread application in various fields of physics, chemistry, biology, and medicine. Such structures make it possible to model processes in cells and tissues, investigate the influence of physical fields on chemical processes, and elaborate new methods of information recording, storage, and transformation.

The investigation of the properties of micellar systems is of great practical importance, since the microheterogeneous structure, in particular, of aqueous-organic solutions can be used to create reaction centers with designed properties, which will make it possible to increase the efficiency of processes associated with the intramolecular conversion of the electronic excitation energy of a molecule. There are a lot of methods for investigating the structurization of water and water-organic mixtures. However, to solve the problems of using the microheterogeneous structure of solvent mixtures to stimulate chemical reactions, it is important to investigate them on model systems. In the present paper, such model systems are the spatial-temporal structures (STS) formed as a result of photophysical and photochemical reactions, whose time characteristics are highly sensitive to a change in the solvent compositions. The STS evolution processes are slow and the structures formed have macroscopic sizes, which makes the system under consideration a convenient object for experimental studies.

The microheterogeneous structure of aqueous alcohol solutions produces a strong effect on the intermolecular energy transfer rate, which in turn affects the behavior of luminescent STSs: a change in the induction period of the appearance of structures and their evolutionary development in space and time is observed. Such a behavior is associated with the micelle formation and solubilization processes proceeding in aqueous alcohol solutions. A considerable decrease in the induction period of the appearance of an STS (< 1 sec) was registered under irradiation by UV light of solutions with a 70% mass content of alcohol in the matrix, which corresponds to a simplified structure of the alcohol–water mixture. The data obtained is in agreement with earlier developed concepts about structure of micellar solutions.

In practice, the application of the STS effect for visualizing the rates of homo- and heterogeneous flows and determining the dispersivity of mixtures and the substance content in solutions seems to be possible.

Keywords: *luminescence, self-organization, spatial-temporal structure, microheterogeneous structure, micellar system, anthraquinone. oxygen,*

Session 12.
Polimer Clay Nanocomposites

Modified Tapioca Starch as a Rheology Modifier in Acrylic Dispersion

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Tapioca starch was modified by esterification reaction using octenylsuccinic anhydride (OSA) to use as an associative thickener. Effect of degree of substitution (DS = 0.01-0.04) of octenyl side chain on rheological properties of modified starch in acrylic dispersion system (ASD) were investigated. At low starch to dry acrylic ratio (0.2:100), shear viscosity at low shear rate of OSA-starch containing ASD system increased with an increase of DS of OSA-starch. Thickening ability and thixotropic behavior of modified starches in acrylic dispersion system was studied at various starches to dry acrylic ratios (0.1 – 4:100). The results showed that modified starches can provide an effective thickening efficiency. Moreover, an optimum concentration of modified starches, giving the highest thickening efficiency decreased as the DS increased. Results of rheological behaviors illustrated that associative networks were formed by hydrophobic interaction between octenyl side chains and acrylic particles in acrylic dispersion system. The rheological properties of modified starches prepared in this study showed a potential in using as an associative thickener in water-based coating system

Keywords: *Tapioca starch, rheological modifier*

Poly(lactic acid) Nanocomposite Coating for Paper Coating Applications

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Poly(lactic acid) or PLA is one of the well-known biodegradable polymer derived from renewable resources such as corn starch, tapioca starch, and sugar cane. PLA is the most extensively utilized biodegradable polyester with potential to replace conventional petrochemical-based polymers. However, PLA has some drawbacks such as brittleness, poor gas barrier etc. Nanocomposite polymers have increased interest due to their characteristics, especially in mechanical and thermal properties. The objectives of this research are to prepare PLA formulations using three different PLAs. The formula giving high gloss coating film were selected to prepare nanocomposite film by incorporated with different amount of various types of organoclays. Physical properties of the PLA coating films were studied and it was found that the PLA 7000D with 0.1% of closite-30B provided decent viscosity for coating process. In addition, the composite coating films showed good physical properties such as high gloss, good adhesion, good hardness. There is a possibility of using the obtained formulation as a paper coating film

Keywords: *Poly(lactic acid), modified clay, paper coatings*

The use of clay-polymer nanocomposites in wastewater pretreatment

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Effluents from olive mills or wineries are unsuitable for discharge into standard sewage treatment plants. In order to allow water reuse in such cases, pre-treatment is needed to avoid the clogging of filtering devices by colloidal matter. Colloidal stability of the effluents is caused by three reasons: (a) sedimentation rate is very slow in small particles. (b) Particles and effluents densities are almost equal avoiding colloids separation (c) Electrostatic repulsion between the charged colloids avoids aggregations.

This study presents use of nanocomposites comprising a clay mineral and a cationic polymer as "coagofloculant", for efficient and fast reduction of total suspended solids (TSS) and turbidity in highly loaded organic wastewaters, in one single step, in minutes. The use of such particles neutralizes the charge of the suspended particles while bridging between them and anchoring them to a denser particle (the clay mineral) enhancing their precipitation. By performing such actions all three effects keeping colloids in suspension are addresses, and very rapid sedimentation of effluents with a heavy organic load can be achieved by means of suitable clay-polymer nanocomposites.

The main features of the nanocomposites treatment are: (I) It is performed in one step, combining flocculation and coagulation in one tank. (II) Raw materials are relatively inexpensive (ubiquitous clay minerals and widely used polymers) and environmentally friendly, since the use of biopolymers can be encouraged. (III) Preparation is simple. (IV) The charge of the nanocomposites must be adapted to the effluent's charge. Unsuitable particles will not yield efficient flocculation. However, since measurement of effluent charge is a simple procedure, this is not expected to present a major problem. (V) A 98% TSS and turbidity reduction is observed by adding suitable nanocomposites to winery or olive mill effluents.

Results show that the proposed nanocomposites can speed up the precipitation process. By reducing clarification time from several hours to minutes, the need for large precipitation tanks, as required for slow treatments, might be avoided, making the wastewater treatment an almost continuous process. Since the sludge obtained is more than 99% organic matter, additional studies are performed on composting processes that may yield material usable as soil conditioner.

Keywords: *coagulation, flocculation, nanocomposites, clay minerals, polymers, effluents, water treatment*

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Session 13.
Polymer Derived Ceramics

Enhanced sintering of SiC using infiltration of preceramic polymer

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The effects of preceramic polymers on the formation and sintering of SiC ceramics were investigated. Polysilazane and Polycarbosilane were chosen as a SiC precursor. Partially sintered SiC specimens were infiltrated with preceramic polymer by vacuum infiltration and ultrasonic stirring. The specimens infiltrated with preceramic polymers were cured at 200°C; 250°C;. And then the specimens were sintered at 2000°C; 2100°C; in flowing Ar atmosphere. The preceramic polymers were converted to SiC during heating. After sintering, the densification behavior and microstructure of the specimens were analyzed. The bending strength and vickers hardness were measured and discussed.

Environmental Barrier ceramic composite coatings

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The economic loss caused by wear, oxidation and corrosion of metals is estimated at several billion EURO per year. Thermal and environmental barrier coatings (TBCs/EBCs) are widely applied to enhance the substrates against aggressive environments. Mainly deposition methods like thermal spraying or CVD and PVD processes are used to generate ceramic coatings.

The interest in polymer-derived ceramics (PDCs) has continuously grown in the last years. They offer a number of advantages over the traditional methods of ceramic processing like versatile shaping or low temperature processing, excellent chemical and thermal stability. The application of the coatings by varnish methods such as dip-coating or spraying is rather simple and more economic compared to CVD or PVD techniques.

Due to the increasing costs for metals, there is currently a need to enhance the performance and lifetime of steel, for example, those employed in exhaust systems, waste incineration plants, metal or glass casting and forming or for applications in the chemical industry. A possible approach is to use the outstanding oxidation and corrosion stability of polysilazane and polysiloxane based composite coatings.

Unfortunately, PDC coatings tend to crack with growing thickness during thermolysis due to their high volume shrinkage and density increase. By adding passive fillers like SiC, Si₃N₄, B₄C, Al₂O₃ and/or active fillers like Ti, Al, Si, TiSi₂, CrSi₂ the volume shrinkage during conversion from polymer to ceramic can be significantly reduced.

Here we present recent results on the development of novel polymer-derived ceramic composite coatings on steel substrates based on the perhydropolysilazane (PHPS) as a bond coat and two different top coating systems based on polysilazane HTT1800 filled with zirconia as passive filler and the glass systems 8470 and G018-311 as sealing agents as well as polyhydromethylsiloxane (PHMS) filled with active ZrSi₂ submicron particles. The PHPS-based bond coat not only increases the adhesion of the composite top coatings but also prevents oxidation of the steel substrates during formation of the dense and thick ceramic top coat during the pyrolysis step. After stabilising the coating slurries, double layers were applied on different steel substrates by dip-coating or spraying. Thermal treatment in air at 700 °C and 800 °C, respectively, leads to dense, well adherent and crack-free composite coatings on steel with a noteworthy thickness up to 100 µm. Especially the polysilazane-based glass/ceramic composite coatings were used to protect mild steel up to 700 °C from oxidation and from very aggressive salt melts at a temperature of 530 °C for more than 200 h. The SiOC top coat is the most effective in oxidation protection of Inconel 617 superalloy at 800 °C. No degradation in the coatings, the metal substrate or the interfaces was observed for times up to 200 h in air.

Net-like demixing structures from preceramic polymers: a study of physical and chemical base parameters of the substrate/coating system

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Ceramic coatings can be applied by a great variety of coating processes. Among them, the polymer derived ceramics processing route exhibits the possibility to create net-like demixing structures, and thermal conversion actually may result in the formation of a highly porous ceramic surface of a coated substrate.

The coating process and the structure formation based on a slurry consisting of two immiscible polysiloxanes, methanol as a solvent and particulate fillers is fairly good controlled. However, less is known about the influence of the substrate material on the structure formation. In this paper basic investigations were carried out on non-metallic (alumina) and metallic (Cu, FeCrAl) substrates. The substrates were polished with different abrasive grain sizes, chemical etching, or electrolytic etched to modify the microstructure and the surface morphology. The samples then were used to measure the contact angle between the substrate and the coating slurry. It was found that the process temperature, adhesion of substrate and the methanol concentration have ample influence on the wetting behavior. This actually results in a variation of the net morphology after the coating process.

Novel carbon nanotube reinforced polymer derived ceramics by FAST sintering processing

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CNT (carbon nanotube) reinforced composite ceramics are supposed to show excellent mechanical properties. CNTs embedded in a ceramic matrix represent a high density of high modulus fibers in a matrix material which may result in high bending strength, high hardness and high fracture toughness. However, problems have been addressed in handling, compounding into a matrix and at least of the price of CNTs. Another disadvantage is the liberation of CNTs into the atmosphere during processing.

A possible way to avoid some of these problems is the in situ generation of CNTs within a ceramic matrix. During the pyrolysis of preceramic polymers hydrocarbons are generated, and the presence of a suitable catalyst in the matrix may be used to convert the evolving hydrocarbons into CNTs. This was shown for a polysilsesquioxane resulting in a composite material composed of a polymer derived ceramic (PDC) matrix with CNTs in open pores or cracks formed during pyrolysis. After milling this composite material, sintering by a field assisted sintering technology (FAST) was shown to result in a CNT reinforced PDC material.

In a very first attempt a series of CNT-PDC composites were manufactured resulting in ceramic bodies with a Weibull modulus of about 17 and a corresponding strength of 109 MPa as measured by a ball-on-3-balls test. The porosity was 10 % and the (micro) hardness exceeded 1400 HV 0.4/5. For comparison, a reference samples without catalyst and thus without CNTs resulted in a higher porosity and a corresponding strength of only 89 MPa. This new combination of the PDC route with in situ CNT formation and FAST processing might be a possible route to manufacture dense PDCs with tailored properties in the SiOC system.

Keywords: *polymer derived Ceramics, carbon nanotubes, FAST sintering*

Novel PDC based composite coating system for application in power plants

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To improve the energy efficiency of e.g. waste incineration plants an increase of the firing temperature up to 700 °C is one of the most important demands. The higher working temperature in combination with the aggressive combustion gases and the abrasive ash particles require a very stable environmental barrier coating to protect the steel components of the heat exchanger. For this application a double layer polysilazane-based environmental barrier coating system for steel consisting of a perhydropolysilazane bond coat and a polysilazane-based glass/ceramic composite top coat has been developed. After application of the layers by simple dip- or spray coating processes and subsequent drying a thermal treatment in air at 700 °C leads to uniform, dense and crack-free composite coatings with a remarkable thickness up to 100 µm and an excellent adhesion to the mild steel substrate. Microstructural analysis by SEM and XRD demonstrates the homogeneous dispersion of the hard ceramic ZrO₂ filler particles within the amorphous PDC matrix, whereas the glass filler seals the coating system. Cyclic oxidation tests up to 700 °C, abrasion tests at 500 °C and corrosion tests in representative salt melts proved the effectivity of the coating system to protect mild steel in harsh environments.

Microstructural Characterization of Meso- and Nanoporous Ceramics by Scanning Probe Microscopy

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Hierarchical meso- and nanoporous structures providing an effective liquid or gas transport via well aligned mesoporous structures and a large surface area for catalytic reactions, for instance in medical applications, biosensors, high-sensitive gas sensors, low-cost dye-sensitized solar cells, solid oxide fuel cells etc. Optical applications of hierarchical surface structures include the huge market of antireflective touch-screen and mobile phone coatings.

The structural characterization of hierarchical structures composed of lower dimensional building blocks requires application of different measurement techniques to cover a wide range of sizes being present within the microstructure. By taking advantage of the scaling property of many physical systems reducing the amount of data required for structural characterization, ceramics with hierarchical pore structure might be adequately characterized by scanning force microscopy (SPM) with resolution from about 10 nm to the micrometer range. SPM provides already a digitized image suitable for numerical evaluation.

In this work, we evaluate the hierarchical porous structure of ceramics and ceramic thin films by determining the power spectral density (PSD) of surface topography recorded by SPM. PSD is a technique that calculates power (roughness amplitude squared) as a function of spatial wavelengths k of the features that are contributing to the surface image. It is suitable for surfaces that can be well approximated by a series of sine waves. The slope of the $\log(\text{PSD})$ vs $\log(k)$ plot at larger k values allows determination of the local roughness exponent α which characterizes the time behaviour of roughness evolution enabling thus to analyse film growth. Investigated samples include sol-gel derived SnO_2 thin films, reactive sputtered $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ thin films and ZrO_2 -based ceramics sintered at different temperatures, all comprising a self-affine surface topography. The PSDs of all samples were fitted to the K -correlation model [1] allowing a straightforward determination of RMS roughness and correlation length (grain size).

Keywords: Porous ceramics, microstructural characterization, scanning probe microscopy, power spectral density

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Microstructure and thermal behavior of novel Al₂O₃/mullite composite materials

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Novel type Alumina-mullite ceramic materials were manufacture from Al₂O₃ particles and a preceramic polymer and an alumina-based sol-gel process was carried for final shaping. In the first step alumina was coated with a preceramic polymer and pyrolysis was carried out in inert atmosphere to generate SiC nanoparticles at the alumina/mullite interphase, which forms during thermal treatment. After pyrolysis the particles were used as particulate fillers in a sol-gel process with aluminum triisopropylate, and the slurries were poured into teflon molds for shaping. After drying and solidification the samples were fired in air and the microstructure and thermal behavior were characterized.

Microstructure formation was analyzed with x-ray diffraction analysis (XRD), scanning electron microscopy (SEM), transition electron microscopy (TEM), and local elemental analysis was performed with energy-dispersive spectroscopy (EDS). X-ray computernanotomography was applied to characterize the thermal shock behavior of this novel material.

In the first part of this paper we report on the microstructure formation and the second part gives some insights into the thermal shock performance of this novel-type alumina/mullite material.

Key words: *preceramic polymers, alumina, mullite, silicon carbide*

Polycarbosilazane coatings on graphite foil used as gasket seal

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Gasket seals are often used in industry and chemical laboratories where a leak-proof installation is needed in order to avoid loss of products or dangerous materials. Many of products transported inside tubular systems in industry are at relatively high temperature avoiding the use of polymer materials as gasket sealing. In the same line, many of these transported materials contain solvents which can attack the polymer sealing therefore limit the use of common polymers in the installation. The solution found to bypass the use of polymers as gasket seal is to use graphite joints. These joints are a sandwich of graphite foil and stainless steel mesh as forming core. The problem that rises with the use of graphite in contact with steel is that, at medium-high temperature (~500°C), occurs an inter diffusion of carbon on the steel structure which produces an adhesion of the graphite gasket on the metallic flange. The point of view of maintenance is that this adhesion increases the time to change each gasket by including also a time to clean and remove the rest of previously adhered graphite from the flange. In order to avoid the adhesion of the graphite on the flange, polycarbosilazane precursor was used as protective coating on the graphite foil surface. After transformation the resulting PDC coating act in two manners, it avoids the direct contact between the carbon and the steel at the same time it allows the sealing of liquids and gases. The leakage test, using Helium, shows that the foil with PDC coating presents compatible results with the standard non-coated foil. In addition, an adhesion test was done and showed that the foil coated with PDC did not adhere to the steel flange. Moreover, the production methods and products are compatible to industrial environment and processes. The results found here show that many wasted time in industry can be saved by using the PDC coating on graphite gasket.

Keywords: *graphite foil, polycarbosilazane, gasket, coatings*

Polymeric and ceramic micro-and nanospheres from preceramic polymers

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Polymeric and ceramic micro- and nanospheres are interesting materials such as building units for novel-type heat storage applications, or as organic/inorganic or light weight filler. A suitable route for sphere formation is based on an oil-water-emulsification process with liquid crosslinkable preceramic polymers, which can be easily converted into porous ceramic materials by pyrolysis in inert atmosphere at temperatures above 800 °C. On the basis of a system composed of a water-crosslinkable poly(methoxymethylsiloxane) and a linear hydroxyterminated poly(dimethylsiloxane) as a source for in situ water generation, studies were carried out to investigate the effects of catalyst, surfactant and temperature during the solidification process on the properties of the resulting spheres, mainly by means of rheology and microstructure analysis. For this purpose, different types of crosslinking active catalysts, surfactants and surfactant mixtures were used and emulsification was carried out with and without external cooling.

Polymer derived ceramic protection coatings for heat recovery materials

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Energy economy is a global issue, and heat recovery may contribute to massive energy saving and CO₂ reduction. In present heat recovery systems the maximum temperature is limited to far below 1000 °C. Temperature increase in those systems would result in an increase in recovery efficiency. When the heat exchanger pipes are filled with materials having a high heat capacity and heat conductivity a further increase in efficiency may be possible. A high temperature material suitable for those purposes is silicon carbide with an open cellular foam-like structure. However, material contact with the housing (pipe) material, which contains transition metals such as nickel, chromium or molybdenum, leads to oxidation of the filling material. In order to protect the silicon carbide filling material from pipe contact protective coatings are necessary.

In this work a protective coating was developed and applied by a dip coating process. A preceramic polymer was dissolved in a specific solvent and silicon carbide foam parts were submerged in the coating system. The coating process was carried out under normal pressure or under vacuum, and the withdrawn specimens were dried. After drying a crosslinking procedure was carried out. Pyrolysis was performed in different atmospheres at temperatures of up to 1300 °C. The as received specimens were characterized by means of x-ray diffractometry, scanning electron microscopy and porosity analysis, and the coatings showed good adherence to the silicon carbide foam. In another test series the coated foam samples were brought into contact with the housing material and heated up to service temperatures. Subsequent characterization showed no diffusion of steel components into the coating or into the silicon carbide material. Even under real conditions in a wet and carbon dioxide-loaded exhaust gas exceeding 1000 °C no significant degradation of the coating was detected.

Structure and performance of polymer-derived bulk ceramics determined by method of filler incorporation

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Polymer-derived ceramics present a viable alternative to conventional ceramics due to the multitude of processing options available. This results in the ability to produce structures as diverse as coatings, cellular materials, fibers, or bulk materials [1]. In order to overcome the intrinsic problem of high shrinkage during polymer-to-ceramic transformation, fillers are generally applied, thus reducing shrinkage and, subsequently, the tendency of crack formation during pyrolytic conversion of bulk materials [2]. The incorporation of particulate fillers into the matrix composed of the polymer precursor represents an important step during processing which strongly affects the resulting properties of the material.

The goals of this study are the investigation and evaluation of various coating methods for the production of polymer-derived bulk structures with high filler contents. Investigations were conducted with two selected polymer/filler systems involving a poly(methyl)siloxane as well as a poly(vinyl)silazane with both active and inert particulate fillers. Three types of coating methods were investigated, including dry mixing, solvent-assisted coating through evaporation, and spray-coating employing a laboratory-scale spray drier. The composite powders obtained were warm-pressed and pyrolytically converted into ceramic materials.

Ceramographic analysis demonstrated significant differences in component distribution and porosity. The processing-dependent pore structure was studied by mercury intrusion porosimetry. In order to evaluate the suitability of the formed parts for structural applications, mechanical properties of the samples were determined, including hardness, Young's modulus, fracture toughness, and flexural strength.

Dry mixing generally led to a poor distribution of constituents, thus resulting in poor mechanical properties. In contrast, a strong improvement of material homogeneity and properties was obtained by the solvent-assisted methods. The results demonstrate the importance of the processing route on final characteristics of polymer-derived ceramics and present options for an improvement of a wide variety of polymer/filler combinations.

Keywords: *polymer-derived ceramics, processing, fillers, polysiloxane, polysilazane, coating, spray-coating*

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Session 14

Processing and Properties of Silicate Ceramics

Anisotropic kinetic of the kaolinite to mullite reaction sequence in multilayer ceramics

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Multilayer ceramics with a composite and organized microstructure were obtained from kaolin and alumina fibers. Such architecture is able to favor a significant improvement of strength and fracture toughness that are very important properties in use of many silicate ceramics. Multilayer composites were shaped by tape casting and sintered by thermo-compression. The anisotropic behavior of materials during sintering was evidenced by dilatometry along 3 directions. The sintering shrinkages are clearly anisotropic in direction parallel to casting (i.e. the kaolin sheets orientation), or in directions perpendicular to layers or to fibers length. Different shrinkages are in correlation with different activation energy for sintering. Simultaneously to shrinkage, mullite growth is also strongly anisotropic, inducing the formation of an organized and micro composite microstructure, where larger mullite crystals are mainly oriented in plane of layer and parallel to alumina fibers. The analysis of kinetic data from thermal transformations shows that the starting reaction mechanism is mullite nucleation, in a similar way to that of many silicate ceramics. The reaction sequence is continued by a strongly anisotropic grain growth, controlled by phase boundary and diffusion mechanisms. It is explained by topotactic transformations at phyllosilicate faces and along alumina arrangements. Mullite growth kinetics is also favored along fiber main dimension, by the anisotropy of the alumina diffusion coefficient. It shows the limited importance of mullite crystallization in microstructural transformation, but it also shows that controlled mullite growth is central in microstructural arrangement. Both multilayer and microstructural arrangements govern the macroscopic mechanical properties since the flexural strength by biaxial fracture load and the fracture toughness by Vickers indentation are significantly increased in comparison to that of silicate ceramics.

Keywords: *multilayer ceramic, organized microstructure, kaolin, mullite*

Application of chemical treated illite clay for development of ceramic products

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The deposits of clays are one of the dominating parts of mineral raw materials of the Phanerozoic sedimentary cover of Latvia. Quaternary clay deposits mostly are of glacial origin and were formed in the glacial melt water basins. The clay minerals dominate by 2:1 lattice mineral - illite (75- 90%) with admixture of chlorite and kaolinite.

The ability to attain the geopolymers of aluminosilicate lattice minerals by proper mix with alkaline solution is well documented [e.g. 1]. The mainly used in the preparation of geopolymers is 1:1 layer lattice aluminosilicates – kaolinite. Attempts to produce fully reacted aluminosilicate geopolymers from 2:1 lattice mineral - pyrophyllite was unsuccessful. Dehydroxylation of pyrophyllite at 800⁰C produce significant changes in the Al coordination, but does not form a viable geopolymer. It was suggested that inability to form viable geopolymers may be due to the retention of the crystalline 2:1 layer structure in pyrophyllite and its dehydroxylated phase.

Investigations on illite-smectite clay and its possible reactivity for geopolymers is less known.

The present study investigates of alkali activated not dehydroxylated illite clay for low temperature ceramic products, characterized by bulk. density, shrinkage, open porosity and compressive strength.

As starting materials it was used Quaternary clay samples taken in the Laza pit (Latvia) and KOH 1M to 6M KOH solution for treatment of clay.

For each treated clay part XRD, IR-spectra, DTA as well as compressive strength measurements and ceramic properties for sintered samples was determined. It is shown that pressure strength of ceramic samples grows with the sintering temperature ranged from 300 to 700 ⁰C and remarkably for the ceramics treated by 3M to 6M alkali solution treated samples. It is pronounced assumption that for chemical treated clay samples in this temperature range remarkably grows amorphous (glassy) phase to promoted increase of strength. although grows the total porosity.

Keywords: *illite clay, chemical treatment, structure, ceramic properties, compressive strength*

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Building Ceramic Based on Sludge

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Because of the rapid evolution in the last decade of science and engineering materials, development of new advanced materials, particularly in construction, we must find solutions, namely, new performed materials, with functional and aesthetic qualities . In recent years, there have been made alternative attempts of reusing various types of wastes, including the incorporation of products in ceramic clay.

The Bodoc local clay and sludge were mixed that to obtain corresponding masses of raw bricks. Currently sludge resulted from the purification stations of the Saint George City. The sludge commonly used in proportions of 5-20 %. Compositional changes of the ceramic mass when the sludge was used it is not very large. The use of sludge as raw material in the ceramic industry does not cause any sanitary risks, if one takes into consideration the high temperature used for produce burning. Also, the sludge radioactivity (of 662 884 Bq/kg) does not present conditions of radioactive contamination at the ceramic construction products.

This theme concerning the achievement of some durable, economic and ecological materials, represents a high-level preoccupation in this domain, the problems related to the ecosystem being permanent issues of the century

Determination of clay minerals species in brick clays and their quantification by Rietveld-refinement on X-ray powder diffraction measurements

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The mineralogical composition of raw clays is often an important but neglected property of the bricks clays. Smectite species, illite and kaolinite type minerals are often not determined in detail. The reason for disregarding their investigation is double: the type of clay minerals is regarded less importance in behavior and the diagnostic investigations are meticulous and time consuming. Oriented specimens are necessary for diagnostic identification of clay minerals based on XRD. But the same specimens can be used for EDS microbeam chemical investigations also. Both methods even used together, often need thermal analysis or cation exchange experiments for complete identification of specimens.

In the present study four different brick clay types are investigated in order to determine clay mineral type, their quantity and to perform clay quantification on global powder specimens by Rietveld-refinement on XRD results. To validate the results, known mixtures were prepared and analyzed in the same manner as unknown samples. ICP-OES investigations were used to double-check the quantitative results.

Raw clay used are carbonate free illitic (Tiszavasvári, Hungary), carbonate rich illitic (Mátraderecske, Hungary) and carbonate rich chloritic (Gușterița, formerly Szenterszébet or Hammersdorf in Romania) and moderate carbonate kaolinitic (Mályi, Hungary). Known mixtures were prepared from high purity minerals, using clay minerals from several Hungarian and Carpathian sources. Rietveld-refinement on mixtures returned the mixed ratios, validating the used approach.

Keywords: *clay mineral diagnostic investigation, EDS microprobe on clay minerals, smectite differentiation, Rietveld-refinement, illite/smectite determination, amorphous calculation, brick clay mineralogy quantification*

Effects of Diatomite on Water Resistance and Strength Development of Waste-based Gypsum Mix

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This work investigates the possibility of making gypsum building materials mainly composed of industrial wastes. Flue-gas desulfurization gypsum (FGD gypsum) from an electric power plant was mixed with diatomite, residues from brewery production, and sludge from roof tile production. Diatomite is a source of amorphous silica while flue gas and roof tile sludge provide β -hemihydrate plaster and other oxides, respectively. The compositions of the waste-based gypsum binders containing these three wastes were formulated and characterized in order to determine the compressive strength, water absorption after curing in air for 7, 14 and 28 days. The properties of the derived gypsum mix were improved according to ettringite formation and hydration reaction. The study suggested that the domestic industrial wastes can become new powerful sources for gypsum-based materials, particularly used for high humidity, indoor environments.

Keywords: *diatomite, waste-based gypsum, water resistance*

Evaluation of ceramic/ceramic (SiC/SiC & Al₂O₃/ Al₂O₃) joint interface prepared via brazing

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Recent investigations show that ceramic/ceramic joints have high potential for applying in industries for shaping and forming of large ceramic components with required geometries and forms. Cost and difficulty in manufacturing complex components, either in one step or by joining of ceramic-metal and ceramic-ceramic, determine inhibition for more widespread use. It is important how to joint component without problems for longer time and to know the role of interface as the main factor of controlling the properties in the joints.

The purpose of this paper was joining two ceramics (SiC to SiC & Al₂O₃ to Al₂O₃) with metal fillers and to investigate the interface of SiC/SiC and Al₂O₃/ Al₂O₃ with the same metal interlayer (Ag-Cu-Ti) and its effect on the properties.

Both joints are performed by brazing method and under certain conditions in a furnace with controlled atmosphere, using the appropriate filler metal. The properties and characteristics of connection has finally been studied by using mechanical test (shear strength test) and microscopic examination (SEM) and phase analysis (XRD) and elemental distribution was conducted by EDAX. Heat treatment was performed (at different time and temperature) according to phase diagram to gain the desirable joint. The results showed that the proper joining of Al₂O₃/Al₂O₃ and SiC/SiC was obtained applying a metal layer of Ag-Cu as well as an active metal of Ti-6Al-4V. The second one was used to increase the wet ability and proper strength.

Microscopic investigations revealed penetration and activation of elements from interface to the bulk of ceramic body and this “in turn” was the major reaction in the joints. Both joints showed the deepest penetration of Ti atoms from interface to ceramics.

According to the XRD results, TiC and Ti₅Si₃ were the most important phases in the SiC/SiC interface and TiO and V₂O₅ in the Al₂O₃/Al₂O₃ interface. The strength of both joints was increased till optimum time and temperature condition and diminished after that by forming of some phases as TiC in (SiC /SiC) and TiO in (Al₂O₃/ Al₂O₃) which inhibit the formation of more strong interface. The optimum time and temperature were suggested to be 900 °C and 90 min for SiC/SiC and 900 °C and 60 min for Al₂O₃/ Al₂O₃.

Keywords: Ceramic/Ceramic Joints, Interface, SEM, XRD, EDAX, strength

The Firing Temperature of Gothic Bricks from PÁC

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The paper deals with the bricks taken from the Gothic part of the church in Pác (Trnava County, Slovakia). A goal of the contribution is an estimation of the maximum firing temperature. The estimation was based on results of thermodilatometric analysis (TDA), differential thermal analysis (DTA) and thermogravimetric analysis (TGA). These analyses were carried out at heating rate of 5 ° C/min in the temperature range of 25 - 1050 °C. The results revealed that the samples did not contain the glassy phase, which means that the bricks were fired at relatively low temperatures, not higher than 1000 °C. It was also observed no signs of dehydroxylations of kaolinite or illite which are completed at 600 - 650 °C. This temperature can be considered as minimum firing temperature. The all three analyses showed decomposition of calcite which is possible if the firing temperature was lower than 750 °C. It can be concluded that the historical bricks were fired at the temperature between 650 °C and 750 °C. Besides that, we could determine that the bricks contained calcite and quartz as fillers. A plastic constituent was illite as follows from the high temperature part of the DTA curve.

Influence of mineralogy and chemical composition of brick clays on uniaxial compressive strength

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The mineralogical composition influences the physical properties of clay bricks through the amount of smectites, illite or kaolinite type minerals which are due to form the fired matrix. Another important group of minerals in brick clays are the carbonates, mainly as calcite and dolomite, since they are cation sources for the metastable dehydrated clay matrix to recrystallize into a stable form. The influence of feldspars is also observed, but in this case the surface of feldspar grains serves as catalyst in Na, K and Ca silicate crystallization as feldspars. The influences of clay minerals and carbonates type and amount have been studied extensively, mainly due to their importance in tile and paving ceramics manufacturing. The influence of primary detrital feldspar grains is less investigated.

Our research focuses on four types of clays. Two are from Tiszavasvári: carbonate free illitic (illite+muscovite ~35wt%) clay with chlorite (4-8wt%) illite/smectite, smectite and kaolinite in lesser amounts (up to 10wt%). Another two are from Mátraderecske, carbonate rich (calcite+dolomite=21-25wt%) illitic (30-37wt%) clays with illite/smectite, smectite and kaolinite in lesser amounts (up to 20wt%). The result of Rietveld-refinement was correlated with the ICP-OES results.

Test pieces fired at 900°C were tested for uniaxial compressive strength. The results show that carbonate rich clays raise the compressive strength, several times higher as for the carbonate free clays. The fired mineralogy determined by Rietveld-refinement revealed that the newly formed minerals are the reason for the different behavior.

Keywords: *compressive strength, silicate crystallization, fired mineralogy, Rietveld-refinement, illite/smectite determination, amorphous calculation, feldspar formation*

Mechanochemical Phenomenons Observed During Grinding of Conventional Brick Clays

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The several years of experiments of author in examination and investigation of conventional brick clays have shown the complexity and subtlety of conventional clay minerals and their technology processes [1, 2, 3, 4]. Generally the conventional brick clays have relative large volume of specific surface areas and very complicated mineralogical compositions. In this work is described the mechanochemical investigation of conventional brick clay minerals from three different region of Hungary. All of these three conventional brick clays had different mineralogical compositions and specific surface areas. The laboratory experiments were made on laboratory pan grinder with grinding times from 10 minutes up to 30 hours. The realized laboratory experiments have shown at all of the 3 different clays an intensive reduction of BET and Langmuir specific surface volume at the beginning of grinding and increasing the grinding time a low values of periodically growth and reductions. Increasing the grinding time the content of mineral Muscovite had decreased and the content of Quartz and Illite have increased considerable. Depending on grinding time the Albite and structureless amorphous minerals also have changed their proportions in the brick clays

Analytical methods applied in this research for tests of material structure were laser granulometry, surface absorption method, 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: *alumina, collision, composite, density, diamond, dynamic, hetero-modulus, metal, silicon-nitride, strength.*

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Oriented silicate ceramic materials: characterization of anisotropic mechanical and thermal properties

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Ceramic shaping processes such as uni axial pressing, tape casting or extrusion lead to orientation of clay platelets in silicate materials. As a consequence, mechanical and thermal properties can be significantly improved in favoured directions. Optimization of thermal treatment is also essential in such mixture to keep the anisotropic microstructure of green specimens after sintering and to control amount, texturation and size of the occurred mullite phase. Moreover, added slight quantities of a second phase (dispersed particles or short fibres for example) can also enhance mechanical properties such as toughness and/or stress to rupture. In this work, two types of silicate ceramic materials are characterized: • a commercial extruded clay paste; • mullite ceramic composites based on kaolinite and alumino-silicate fibers (200 μ m length). Samples (substrates with 1 to 4 mm in thickness) obtained by tape casting and thermo compression exhibit kaolinite platelets and fibers preferentially oriented in the substrate plane and in the casting direction. For the extruded material, anisotropy in macroscopic physical properties has been highlighted by thermal conductivity and Young's modulus measurements denoting a decrease of isotropic degree when the temperature of sintering increases. Concerning multi-layered mullite composite materials, it has been shown that mechanical properties are correlated with the organization degree of mullite crystals, due to the formation of an interconnected mullite network in the microstructure. The anisotropy of the elastic properties has also been evidenced by a difference between Young's modulus values in directions parallel and perpendicular to the casting direction. In comparison to similar silicate ceramics, addition of a low fibre content (5wt %) significantly increase strength and toughness.

Porous clay ceramic granules and their sorption ability

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Sorption ability of illitic clays is lower to sorption ability of smectitic clays. Practical use of natural clays has some problems concerned with turbidity of cleaned liquid. This shortage may be eliminated by purification of waste water with sintered clay granules. Granules of two types of illitic clay by additive of 2wt% of combustible additives were formed from plastic body and after drying sintered at temperatures 700 – 1000°C. Such interval of sintering temperature furnishes some chemical activity of granules because new crystalline phases are not formed and porosity of obtained material is high. Water immersion of such granules has different pH. Sorption ability of granules was determined concerning to ionic and molecular substances. Physical sorption ability of molecular substances depends on the porosity of granules. The highest value of sorption has granules sintered at temperature 700 - 800°C and depending on the type of clays and molecular substance reaches 25 mg/g. Dependence of chemical sorption ability like physical sorption is highest for the granules sintered at 700 - 800°C temperatures, but the sorption value is lower and reaches 18 mg/g. The surface area determined by mercury porosimetry is the highest for granules sintered at these temperatures and reaches 30m²/g.

Key words: *clay, ceramic granules, porosity, surface area, sorption ability*

Properties of Porous Mullite Ceramics Doped with WO₃

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Ceramics based on alumina oxide (Al₂O₃) and silica oxide (SiO₂) have a number of properties. From literature we know that such properties are high refractoriness, high bending strength and high creep resistance, good chemical and thermal stability. Therefore these ceramics can be used in electrical, constructional and thermal engineering. Mullite (3Al₂O₃·2SiO₂) phase is the important stable crystalline phase in the aluminosilicate system that defines several properties, for example, the refractoriness of ceramics. Refractory ceramics with high porosity serve as a heat insulator and constructional material. Our porous mullite ceramics were obtained by slip casting of suspension of raw materials. The metallic aluminium powder was used for pores getting as porous agents in chemical reaction of Al with water by hydrogen gas evolution reaction and solidification of suspension. Some problems as ceramics high shrinkage after sintering and sometimes high bulk density need to be solved.

Mullite ceramics were fabricated from Al₂O₃, SiO₂ and kaolin with WO₃ addition and sintered at the temperature of 1200°C. In all samples the Al₂O₃ and SiO₂ were in 2.57:1 ratio, because that was conformed to mullite stoichiometric compositions (3Al₂O₃·2SiO₂). The types of alumina oxides were α-Al₂O₃ (d₅₀=4μm) and γ-Al₂O₃ (d₅₀=80μm). Ratio of α-: γ-Al₂O₃ was 1:3. 30 wt% of kaolin was as additional component of Al₂O₃ and SiO₂. The aim of the work was to analyze the influence of WO₃ on the densification behaviors, porosity, mechanical properties, thermal stress of ceramic.

Keywords— kaolin, alumina, silica, porosity, WO₃, tungsten oxide, mullite, mullite-coriundum, sintering temperature, refractory ceramics

Rheological Properties of Clay-based Compounds

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The production of the traditional fired brick product demands the preparation and formation of the largest volume of plastic ceramic pastes. Additive materials are often mixed into the clay based compounds in order to change the behaviour of the clay or to improve the properties of the fired products such as thermal insulation. Effects of organic and non-organic additives on the rheological behaviour of clay-based compound were investigated in this study. As pore forming additives saw dust and ground sunflower seed shell, while as opening agent sand and ground brick dust were mixed to the clay matrix in 0, 3, and 5wt%. The water content value was set to 20% and 24% of the compounds. The investigation was performed by capillary rheometer. Results showed that the clay and as well as the compounds behaved as Bingham fluid in the measured interval. At 20% water content the pore forming additives and the ground brick dust increased the Bingham viscosity while the high purity quartz sand decreased it. The capillary flow showed mainly plug flow with extensive wall slip. By the help of sedimentated ($d < 2\mu\text{m}$) clay minerals content of the clay, the slip layer was characterised by the layer thickness which was calculated from the data of measurements with capillary and rotational viscosimeter. The slip layer thickness showed a tendency to reach a limit value by increasing the extrusion speed.

Keywords: *brick, additives, Bingham flow, wall slip*

Study on sintering and properties of Si₃N₄ (SHS)/ α -SiC multiphase ceramics

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Si₃N₄ powder synthesized by Self-propagating High Temperature Combustion Synthesis Method (SHS) powder with 20 w% α -SiC powder and 14 vol% (Y, La)₂O₃ : AlN as sintering additive were pressureless sintered at 1780°C under 1 atm. N₂ for 3 hrs. The property of Si₃N₄/ α -SiC products was studied. SEM, EDX, XRD were used to analysis and reveal the relations of the composition, microstructure and mechanical properties. Experiment results showed that the fully dense composite of Si₃N₄/ α -SiC was obtained with >99% relative density. The bending strength achieved to 730MPa. The fracture toughness and the hardness are 5 MPa·m^{1/2} and 12GPa respectively. SEM micrograph showed that more elongated grains of β -Sialon formed and homogeneously distributed with SiC grains and liquid phase. EDX shows Si, Al, and N were identified from the elongated crystals indicating the β -Sialon formation. XRD analysis showed β -Si₃N₄ as main phase and a little β -SiC, as well as some Melilite formed in the Si₃N₄/ α -SiC composite sintered.

Keywords: SHS Si₃N₄, α -SiC, multiphase ceramics, properties,

Synthesis of Al_4SiC_4 powders from kaolin grog, aluminum and carbon black by carbothermal reaction

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Aluminum silicon carbide (Al_4SiC_4) has very good properties on high temperature, which may be used as structural ceramics and non-oxide refractories. In this paper, the synthesis of Al_4SiC_4 used as natural oxide materials by carbothermal reduction was investigated in order to explore the synthesis route with low costs. The samples were calcined by using kaolin grog, aluminum and carbon black as raw materials with the selected proportion at the temperature from 1773 to 2073 K for 2 hours under flow argon atmosphere. The phase composition of reaction products were determined by X-ray diffraction. The microstructure and elemental composition of different phases were observed and identified by scanning electron microscopy and energy dispersive spectroscopy. The mechanism of reaction processing was discussed. The results show that the phases of samples calcined at the temperature below 1873 K compose of Al_2O_3 as well as a little amount of SiC, SiO_2 and unreacted aluminum. When the temperature rises to 1973 K, $\text{Al}_4\text{O}_4\text{C}$ whiskers and particles are formed, while the content of Al_2O_3 decreases. As the temperature is increased further, $\text{Al}_4\text{O}_4\text{C}$ gradually transforms into Al_4SiC_4 . When the temperature reaches 2073 K, $\text{Al}_4\text{O}_4\text{C}$ essentially completely disappears, and hexagonal plate-like Al_4SiC_4 powders with the size of 150-200 μm and the thickness less than 10 μm are obtained.

Keywords: Al_4SiC_4 , Synthesis, Carbothermal reaction, Mechanism

The effect of acid boric addition on sintering kinetics of ceramic tiles

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In this study, the effect of boron oxide addition on the sintering kinetics of ceramic tile compositions was investigated. Several amounts of (0, 5, 10, 15 wt%, B₂O₃) acid boric was added at selected ceramic tile composition and bodies were fired in a laboratory type furnace with a heating rate of 10° C/min up to 1140, 1180, 1200 and 1250°C. The phase and microstructural development of the bodies were characterized by XRD and SEM, respectively. Sintering activation energies were determined according to the bulk density. The results showed that, the increasing acid boric content has been observed to decrease sintering activation energy. Moreover, the incorporation of acid boric on ceramic tile compositions enables lowering sintering temperature and/or shortening the firing cycle as a consequence of reduced activation energy.

Keywords: *Acid boric; Ceramic tile, Sintering kinetics; Activation energy.*

The Effect of Adding TiO₂ on Synthesis of Al₄SiC₄ powder

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Al₄SiC₄ is one of the promising high-temperature ceramics for many engineering applications because of its low density (3.03 g/cm³), high melting point (~2353 K) and excellent oxidation resistance. Due to the desirable properties, several methods for synthesis of Al₄SiC₄ have been developed; most of the methods require relatively expensive element powders or humidity-sensitive Al₄C₃ powders, which limited the industrial application of Al₄SiC₄. Recently, some researches have been performed about the Al₄SiC₄ powder synthesis from the raw mineral materials. However, the impurities in the raw materials will be an inevitable influence on the synthesis of Al₄SiC₄. In this work, the effect of adding titanium oxide on synthesis of Al₄SiC₄ was investigated by X-ray diffraction and scanning electron microscopy. The powders of aluminum, silicon and graphite were mixed with the molar ratio corresponding to the chemical composition of Al₄SiC₄, and then a small amount of TiO₂ was added into the mixtures (0, 3%, 6%, 9%, respectively). The mixtures were heated at 1973 K in argon, and the Al₄SiC₄ phase was obtained. Conversely, the two phases, Al₄O₄C and TiC, were detected when the increasing of additive amount of TiO₂ was made, and the grain sizes of Al₄SiC₄ were refined from 10~20μm to 1~5μm at the same time. Further, the morphology of Al₄SiC₄ without addition of TiO₂ is granules structure, but changes into tabular structure after adding TiO₂.

Keywords: *aluminum silicon carbide, aluminum oxide carbide, titanium oxide, synthesis, microstructure*

The Effect of Si contents on the reaction-bonded Si₃N₄/SiC composite ceramics

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The Effect of Si contents on reaction-bonded Si₃N₄/SiC composite ceramics fabricated by pressureless sintering was investigated. Si₃N₄/SiC composite ceramics were sintered at 1873 K under nitrogen atmosphere by using SiC powders (1.5μm), Si powders (74μm) with different contents 37~60wt% and additives Y₂O₃ as raw materials. The phases, microstructure and mechanical property were characterized by X-ray diffraction, scanning electron microscopy and compressive strength tests. The results demonstrated that when the content of Si powders was 55wt%, the more dense samples with the bulk density of 2.41 g/cm³ and the higher compressive strength of 317 MPa could be obtained.

Keywords: *reaction-bonded, Si₃N₄/SiC, Si content, micro-composite*

Typical Defects on Automobile Windscreens at the Interfaces of Silver Coatings, Copper Filaments and Glasses

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The consequences of defects in the micro- and nanostructures of fixing thin film coating layers or heating filaments and glasses at their interfaces can cause strong reduction of efficiency of automobile windscreen heating. To avoid this undesirable efficiency fall in heating of automobile windscreens, the layered fixing thin films, the conductive coatings, heater filaments, copper clips and glasses must have excellent adhesive strength at their interfaces and as good as possible material structures in micro and nano-scales [1, 2].

During the investigation of micro and nanostructures as well as adhesive and scratch strength of fixing thin films, silver coatings and copper heating filaments several typical defects were observed by the authors. These typical defects are interruptions, cracks, bubbles, micro and nano pores, non-permanent thicknesses and diameters and gaps between the surfaces of coatings and glass.

To examine the material structures and adhesive strength of thin film coatings and heating filaments on glass automobile windscreens optical digital mechanical scratch tester, scanning electron microscopy and energy dispersive spectrometry were used. Digital image analysis was applied to microscopy results to enhance the results of transformation

Keywords: *coating, copper, filament, glass, interface, scratch, strengths.*

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Use of Thermal Imaging in Characterization of Ceramic Fiber Structures

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High porosity rigid fibre ceramics are used in various high temperature, and harsh-environment applications, because of their good chemical stability, low price, and light weight. Many of these fibrous products are manufactured by a slurry process that needs to be carefully controlled. Lack of control in this process may lead to a variation in production quality and eventually cause functional defects such as quick degradation of mechanical, thermal, or other relevant properties of the product.

We have sought plausible methods to quickly analyze the structural integrity and distribution of fibres in a porous and rigid ceramic product, formed in a slurry process. A thermal imaging system that we are developing could possibly be used in quality control of the manufacturing process, even with large size products. In our system, hot air is allowed to flow through product's pores while the product is imaged with an infrared camera. This method is based on our finding that hot air heats certain areas of the product slower. This is most likely caused by structural variations.

In the beginning the exact reasons for deviation of heating rates among the different areas need to be cleared out. In order to do that we will conduct analyses on the differently behaving areas and find correlations between certain structural properties. This will hopefully shed light on the phenomena and may later be used in adjusting the production parameters or determining the life time of these fibrous products.

Keywords: *Thermal Imaging, ND-Testing, Fibre ceramics*

Session 16.

Nanomaterials for Environment and Health

Bacterial Growth on a Superhydrophobic Surface Containing Nanoparticles

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The antibacterial effect of silver can be exploited in the food and beverage industry and medicinal applications to reduce biofouling of surfaces. Very small amount of silver ions are enough to destructively affect the metabolism of bacteria. Moreover, superhydrophobic properties could reduce bacterial adhesion to the surface.

In this study we fabricated superhydrophobic surfaces that contained nanosized silver particles. The superhydrophobic surfaces were manufactured onto stainless steel as combination of ceramic nanotopography and hydrophobication by fluorosilane. Silver nanoparticles were precipitated onto the surface by a chemical method. The dissolution of silver from the surface was tested in an aqueous environment under pH values of 1, 3, 5, 7, 9 and 11. The pH value was adjusted with nitric acid and ammonia.

It was found that dissolution rate of silver increased as the pH of the solution altered from the pH of de-ionized water to lower and higher pH values but dissolution occurred also in de-ionized water. The antimicrobial potential of this coating was investigated using bacterial strains isolated from the brewery equipment surfaces. The results showed that the number of bacteria adhering onto steel surface was significantly reduced (88%) on the superhydrophobic coating containing silver. The superhydrophobic coating without silver did not reduce the number of adhered bacteria.

Butterfly wing scale nanostructures as selective optical gas / vapor sensors

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Photonic crystals are periodic dielectric nanocomposites which have photonic band gaps that forbid the propagation of light within certain frequency ranges. This property enables one to manipulate light with amazing facility. Such nanoarchitectures frequently occur in butterflies and beetles [1].

The optical response on chemical changes in the environment of a biological photonic crystal type structure was first measured on Morpho butterflies [2]. The spectral change of the reflected light depends on the composition of the ambient atmosphere and also on the wing nanostructure [3]. In this work we show the results of recent chemical sensing measurements on nine Polyommata species with dorsal blue coloration. Their color is generated by similar “pepper-pot” type nanoarchitectures which can be used as low cost, and selective gas / vapor sensors. The low cost is provided by the very simple way in which these nanoarchitectures can be produced by rearing butterflies. These dorsal colors on Polyommata specimens are highly optimized by evolution and stable due to the role they have in the sexual communication of butterflies [4]. As we showed in our earlier work, the “pepper-pot” type nanoarchitecture in these butterflies exhibit species specific characteristics [4], associated with species specific color [5].

Experiments were carried out changing the concentration and nature of test vapors while monitoring the spectral variations in time. Proper data processing results gas-selective and concentration dependent signals. Our work shows a way to a prospective integrated biological - optical sensor combining light weight and low power with environmental friendly production.

Keywords: butterfly wing scale, nanoarchitecture, photonic crystal, gas sensor

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Control of the Oxygen Storage Capacity of Ceria for Environmental Cleanup and Human Health

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Since ceria (CeO_2) possesses the oxygen release-absorption ability (oxygen storage capacity: OSC), it has been used as a co-catalyst of the automobile 3-way catalyst to cleanup automobile exhausts. In this application ceria is required to possess high OSC, high specific surface area and high thermal stability. Ceria can also be used as an UV-shielding material for human health, because of the adequate bandgap energy. When used as the UV-shielding material, ceria is required to be nanosized to improve the visible-light transparency and low OSC to decrease the catalytic activity for the oxidation of organic materials. The OSC of ceria is considered to relate with the stability of crystal structure of ceria. The ideal $r(\text{M}^{n+})/r(\text{O}^{2-})$ ionic size ratio of an eight-coordination metal oxide is 0.732, but the value of $r(\text{Ce}^{4+})/r(\text{O}^{2-})$ of the fluorite structure ceria, is 0.703, which is smaller than that of the ideal value. To take on a more stable eight coordination structure, Ce^{4+} would have a tendency to be reduced to larger Ce^{3+} by releasing oxygen. Therefore, it is expected that the OSC of ceria can be increased by doping with smaller size of metal ion, and decreased by doping with larger size and/or lower valence metal ion.

According to such design concept, ceria nanoparticles possessing high OSC were fabricated by the solvothermal reaction by doping with smaller size metal ion, such as Zr^{4+} , Sn^{4+} , etc. The Zr^{4+} and Sn^{4+} co-doped ceria also showed excellent thermal stability, therefore, is expected to be applied to form advanced automobile 3-way catalysts. On the other hand, the oxidation catalytic activity of ceria could be greatly reduced by doping with Ca^{2+} . In addition, Ca^{2+} -doped CeO_2 nanoparticles showed lower photocatalytic activity, consequently, are now commercially supplied as a new UV-shielding materials.

Keywords: *Ceria, automobile exhaust gas purification catalyst, UV-shielding, oxygen storage capacity*

Photocatalytic Active Titanium Dioxide Nanopowders: Synthesis, Photoactivity and Magnetic Separation of the Powder

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Nanocrystalline titanium dioxide (TiO₂) photocatalyst powders with high specific surface area (115-180 m²/g) were synthesized through sol-gel route as a function of acidity of the sol at a low-temperature (50° C). The structural properties of the produced powders were determined with X-ray diffraction (XRD), transmission electron microscopy (TEM) and nitrogen adsorption tests. The photocatalytic properties of the powders were studied with methylene blue (MB) discoloration tests. After discoloration tests, TiO₂ was coagulated with magnetite particles by using FeCl₃·6H₂O at suitable pH value. Magnetic separation of coagulated TiO₂ and magnetite was carried out by using a permanent magnet.

The obtained results showed that the relative amounts of anatase and rutile phases depend greatly on the acidity of solution. In the diluted acid solution only anatase phase was formed. The more concentrated acid solution produced the mixture of anatase and rutile phases. When the acid content was still increased the product was pure rutile. The MB discoloration tests showed that photocatalytic activity depends on the phase structure as well as the specific surface area of the synthesized TiO₂ powder. The magnetic separation of TiO₂ –magnetite coagulate from discolored MB solution proved to be most efficient around pH = 8.

Preparation and characterization of CeO₂-ZrO₂-M_xO_y (M=Sn, Al) solid solutions for the three-way catalytic application

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Ceria (CeO₂)-based materials have been recognized as an important component of the three-way catalysts (TWCs) because of their excellent oxygen storage capacity (OSC). The major role of ceria-based materials is the OSC, maintaining an air/fuel ratio around 14.7 during engine operation, since TWCs have high pollutant conversion efficiency only under a narrow operation window of the air/fuel ratio. Since 1990s, CeO₂-ZrO₂ solid solutions have gradually replaced pure CeO₂ as OSC materials in the TWCs to reduce the emission of toxic pollutants (CO, NO_x, hydrocarbons, etc.) from automobile exhaust, because of their enhanced OSC performance and improved thermal stability at elevated temperatures.

The redox property of CeO₂ can be greatly enhanced by incorporation of zirconium ions (Zr⁴⁺) into the lattice to form a solid solution. Recently, many researchers have paid much attention to prepare Ce_{0.5}Zr_{0.5}O₂ nanoparticles with the homogeneity of the composition, good dispersion of particles, narrow particle size distribution, better crystallinity and high surface area in order to improve OSC and redox property for their catalytic applications. Although Ce_{0.5}Zr_{0.5}O₂ solid solutions have been studied extensively, there are few reports on the preparation of CeO₂-ZrO₂-M_xO_y in the literature. Considering the smaller cation radius of Sn⁴⁺ (0.077 nm) and Al³⁺ (0.059 nm) than those of Zr⁴⁺ (0.084 nm) and Ce⁴⁺ (0.097 nm), the incorporation of Sn⁴⁺ and Al³⁺ into Ce-Zr solid solutions may enhance the oxygen release reaction to form larger Ce³⁺. In the present work, for the first time, we describe the preparation and characterization of CeO₂-ZrO₂-M_xO_y (M=Sn, Al) solid solutions via a facile solvothermal route. The further experiment results show the introduction of tin and aluminium ions enhances the thermal stability and OSC even after calcination at 1000°C for 20 h. The OCS of CeO₂ and Ce_{0.5}Zr_{0.5}O₂ prepared via the same method is compared.

Keywords: *Ceria, three-way catalysts, solid solutions, oxygen storage capacity, thermal stability,*

