

The 25th International Baltic Conference of
Engineering Materials & Tribology



ABSTRACTS BOOK



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The 25th International Baltic Conference of Engineering Materials & Tribology – BALTMATTRIB 2016 continues the tradition of the regular meetings held annually in one of the Baltic states by addressing fundamental research topics as well as latest progress and developing areas on the leading edges of materials engineering and tribology. This year conference is devoted to advanced engineering materials, powder materials and powder metallurgy, coatings and surface engineering, mechanics and tribology of materials.

BALTMATTRIB 2016 will be held during November 3-4, in Riga, Latvia.

The Conference will consist of 2 plenary lectures, as well as 33 oral and 46 poster contributions.

A student speech contest (20 participants) will be held during the Conference. Contest will be supported by the Latvian Materials Research Society which will provide prizes for the three best presentations.

The peer-reviewed and accepted manuscripts will be published by the Trans Tech Publications in online access journal “Key Engineering Materials”.

With Kind regards,

A handwritten signature in blue ink, appearing to be 'Dagnija Loca', written in a cursive style.

Dr.sc.ing. Dagnija Loca

President of the Latvian Materials Research Society

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Tribological Behavior of Phosphate Conversion Coatings

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INTRODUCTION

Phosphate conversion coatings are widely applied on steel, non-ferrous metals and metallic coatings as corrosion protection and bonding agent for paints since the early 20th century [1, 2]. Therefore, phosphating is a well-developed surface treatment process for various technical components. These coatings are also interesting candidates for various tribological applications due to their non-metallic nature and structure which can act as a base and carrier for lubricants. However, the tribological behaviour of such coatings is only poorly investigated and therefore little understood.

EXPERIMENTAL METHODS

This work is focused on the damage and wear mechanisms of phosphate coatings which were deposited onto steel substrates by a wet-chemical process. Tribological characterisation comprising scratch testing and reciprocating sliding experiments under dry and lubricated conditions revealed the early-damage mechanisms as well as the long-term friction and wear behaviour.

RESULTS AND DISCUSSION

A typical surface of a phosphate conversion coating on C-steel is depicted in Fig.1. This phosphate coating forms a dense layer of clearly defined crystal-like sub-structures with a size of approximately 10 µm. The tribological experiments showed a dependence of the wear resistance of the coating on the stability and topology of the coating. A modification of the substrate surface by machining, different cleaning procedures or chemical surface treatment prior to deposition can alter the surface morphology of the coating. Therefore, it can be shown that the surface treatment prior to the deposition plays a crucial role in the mechanical stability and tribological performance.

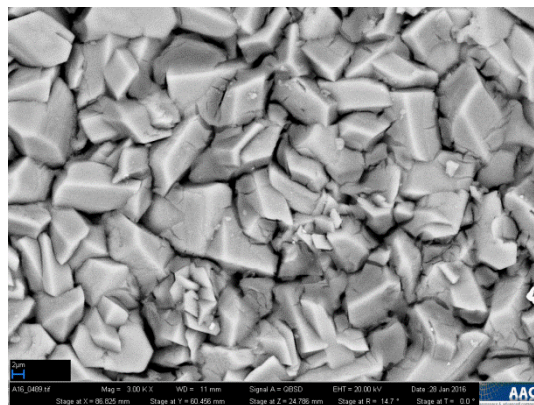


Fig.1. SEM image of a typical phosphate coating surface

CONCLUSION

The deeper understanding allowed to increase the tribological performance in terms of controlled friction and wear resistance of technical components. This way, measures in reduction of seizing and increase of lifetime can be developed.

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ACKNOWLEDGMENTS

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Formulation and characterization of PAI-PTFEcg antifriction coatings

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INTRODUCTION

PTFE fine powder can be radiation modified by β - or γ -beam generating persistent radicals and functional groups (COF, COOH) [1, 2]. Hence, the so treated powders can be linked covalently with several thermoplastics. A chemical grafting of PAI is successful by reactive extrusion in melt [3]. Subject of the paper is the use of chemically grafted (cg) PAI-PTFE for the formulation of sliding lacquer dispersions, their application to steel blanks followed by a characterization of film properties and their tribological behavior.

EXPERIMENTAL METHODS

PAI Torlon 4000 T (Solvay) was grafted with γ -irradiated PTFE TF 2025 (Dyneon) by reactive extrusion in a Haake Rheocord PolyLab 300 p. Then, the extrudate was dispersed in a Dispermat[®] LC30. Subsequently resulting dispersions were characterized by transmission light microscopy (Olympus BX51) and rheological measurements (Anton Paar PP 50). After application of the lacquers to steel sheets and following curing procedure the film properties were characterized with regard to mechanical properties and adhesive strength (Impact/ rev. Impact, Erichsen cupping). In addition tribological fundamental testing was carried out according to Siebel/Kehl to determine the coefficient of friction μ and linear wear rate W_l . Finally, the favored lacquer formulation was applied to a four-shaft sliding bearing by spraying and then tested in a turbine bearing test rig with particular focus on long-term stability and dry-running properties.

RESULTS AND DISCUSSION

Chemical grafted PAI-PTFE-materials result in stable, shear thinning dispersions and homogeneous films, which show an outstanding flexibility and adhesive

strength. The grafting itself was proved by FT-IR-measurements. For fundamental tribological tests the lacquer was applied by doctorblade or, after thinning, by spraying. However, the thinning also changed the rheological behavior. The stability of the films during tribological testing depends on the pretreatment of the substrate. By spraying to phosphatized steel surfaces stable films were reached above 15 μm film thicknesses. The W_l -values are between 4-12 μm and reach the highest level within few minutes after start. The friction coefficient is in the range between 0.03-0.045. Final application tests showed no wear after 5000 load change at 2 MPa.

CONCLUSION

Chemical grafted PAI-PTFE sliding lacquer films could be useful to replace white metals in hydrodynamic sliding bearings.

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Microstructure and Properties Characterization of Polycrystalline Ni-base Superalloy EP718

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INTRODUCTION

The purpose is to analyze the effect of electric upsetting on the microstructure improve and properties evolution which increase the high cycle fatigue (HCF) strength of the polycrystalline Ni-based superalloy EP 718. The electric upsetting process contains a rapid Joule heating and severe plastic deformation simultaneously. It is well known that the cracks forming take place mainly by eroded grain boundaries [1] and mainly in naval aviation. We show by HCF testing, that the fatigue cracks were formed via nanoporosity and this is the reason for fracture.

EXPERIMENTAL METHODS

The samples were processed at deformation stress $\delta=244$ MPa and current density $i=38$ A/mm². The heating rate $\Delta t=130$ °C•s⁻¹, heating time up to deformation starting $\tau=7$ s, deformation starting temperature $t_1=910\pm 5$ °C, maximal temperature inside of the sample deformed part was increased to $t_2=1020\pm 5$ °C. At follows the processed preforms were die forged on press without (or with) additional furnace heating and heat treated. The HCF tests of finished blades of 6 pieces for each production technology method, was performed on an electrodynamics shaker at ambient temperatures with frequency rate of F1, 0 = 1110-1180 Hz. We review the changes in the microstructure depending on processing route by use of the high resolution scanning electron microscope (HR SEM - Gemini, LEO, Supra 35), energy dispersion spectroscopy (EDS), and X-ray diffraction (XRD - D5005, Bruker AXS) techniques (Database: ICDD PDF-4+2014).

RESULTS AND DISCUSSION

The nanoporous on grain boundaries were eliminated during processing (Fig. 1). Microstructural defects improvement mechanism includes the temperature increase on grain boundaries, influence the diffusion on grain boundaries and influence the solid-solid phase transformations and new grains forming.

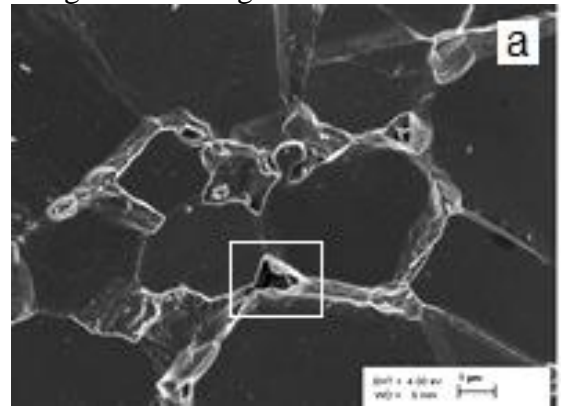


Fig.1. SEM picture of initial microstructure of EP 718E alloy

CONCLUSION

HCF strength was increased from 300 MPa to 560 MPa and life extension for $2 \cdot 10^7$ cycles was increased up to 5 times. During HCF testing the load was step-by-step increased by 40 MPa as result of load increase after $2 \cdot 10^7$ cycles.

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Optimisation of plasma nitrocarburising for reducing wear in dry sliding contacts

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INTRODUCTION

Nitrocarburising is often the selected surface treatment for reducing wear in sliding surfaces operating under starved lubrication or even non-lubricated conditions, such as metal sheet forming tools, engine shafts, valves and pistons. The reason lies in the affordability and the technological maturity of the process, which offers a high flexibility in order to enhance hardness, adhesion and corrosion resistance. The nitrocarburised layer can significantly increase wear resistance of the treated part, allowing its operation under more severe conditions and simultaneously extending its lifetime. The main reason for the failure of the nitrocarburised layer under dry sliding conditions is typically the fracture of the nitride case due to the exceeded tangential stresses. This is related with the hardness and the thickness of the compound layer and the diffusion zone, their microstructural properties, and the topographical properties of the nitrocarburised surface [1]. The aim of this study is to gain deeper understanding of the relation between nitrocarburising process parameters and the resulting tribological performance under dry sliding conditions.

EXPERIMENTAL METHODS

Toolox 33 steel substrates were plasma nitrocarburised using different process parameters. Afterwards, tribological experiments were performed on nitrocarburised samples under dry oscillating sliding motion against 100Cr6 cylinders. Micromechanical properties of the nitrocarburised layers (e.g. surface roughness, compound layer thickness, hardness depth profiles, nitride-hardening

depth) were analysed and related to their friction and wear response.

RESULTS AND DISCUSSION

In Figure 1 wear depths measured on different nitrocarburised samples are presented. It can be seen that the wear response due to the use of different plasma nitrocarburizing process parameters has a very pronounced impact on wear depth, with values ranging from around 2 to 23 µm.

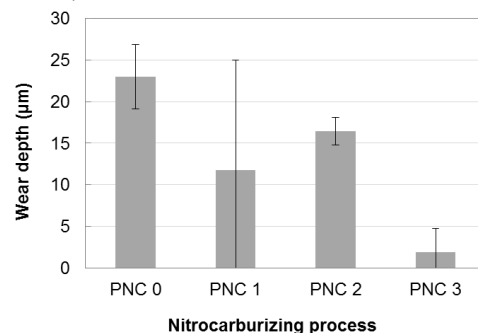


Fig.1. Wear depths on different nitrocarburised samples

CONCLUSION

This study showed that the selection of appropriate processing parameters can drastically change the tribological performance of the nitrocarburized samples and provide a reduction of the wear depth of over 80%.

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Study of Surfaced Inserts for Wood Machining

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INTRODUCTION

An objective of this study was to find the most suitable cutting tools for machining of oak wood grown in Lithuania. This paper cover tests of two commercial cutting inserts made of high speed tool steel (CT01M-LA2 and 8X6FT) and two experimental inserts (EI) made by surfacing using submerged arc welding (SAW) technique and mixture of alloying elements spread on the surface under the industrial flux.

EXPERIMENTAL METHODS

The base material for surfacing was cheap plain carbon steel provided as an 8 mm thick plate. The surfacing process was performed on 40x100 mm samples in a single pass using SAW technique with alloying materials mixture (~ 6 g) spread on the surface under the flux. The SAW was carried out with an automatic welding device (torch MIG/MAG EN 500 78). Blended powder of materials was spread on the surface of the base metal and fused by metal arc. Additional standard flux AMS1 (GOST 9087-81) was used to shield and to prevent the welding area.

One testing lot of surfaced inserts were heated at the temperature of 1100 °C afterwards hammered in order to examine influence of plastic deformation on the wear properties of tool. Mechanical behaviour of surfaced experimental inserts and commercial inserts was assessed in the terms of hardness and wear properties. The most important characteristics selected for the defining of wear behaviour of inserts were cutting edge radius ρ (μm), edge recession A_{μ} (μm), nose width b (μm), and cutting power P (W) [1]. The actual values of edge rounding radius were assessed on lead imprint method using optical microscope Nikon Eclipse E200, digital camera Lumenera Infinity 1. Software Infinity Analyze Release 5.0.2 was used for analysing and evaluation of obtained results with the accuracy of $\pm 2 \mu\text{m}$.

RESULTS AND DISCUSSION

The wear performance of experimental and standard inserts was accomplished on the typical industrial thickness planer (SR3-6) with a face milling cutterhead using oak samples as workpiece. The wear measurement was based on the determination of the edge recession after every defined cutting length (effective cutting path of blade). Cutting edge radius of surfaced and afterwards hammered insert EI1 showed the lowest wear evolution when compared with commercial inserts – 5.22 μm . The results of cutting edge test are in line with those of previous test – tendency of wear of EI2 inserts was the same – 5.35 μm . Cutting edge radius of industrial insert made of CT01M-LA2 was 11.2 μm , while the maximum wear values were achieved on 8X6FT inserts – 19.8 μm . The smallest edge recession was noticed testing surfaced insert EI2.

CONCLUSION

The lowest cutting edge radius occurred on surfaced and additionally plastically deformed insert EI1; cutting edge radius after 3200 m of cutting length was 5.22 μm , for not hammered EI2 – 5.35 μm . In summary, these results show 3–4 times lower wear than commercial tools.

The most obvious finding to emerge from the analysis is that the relatively hard coatings (55-57 HRC) surfaced on a soft plain carbon steel can replace some commercial inserts made of high speed tool steels for oak wood machining, reducing friction and wear of wood cutting tool.

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Transformation metals and alloys to the composite materials

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INTRODUCTION

It is complicated to create new materials with high complex of physical-mechanical properties on the base of traditional approaches. Commonly used technologies are either not able to provide the desired level of properties (doping, modification), or their use is expensive and energy-consuming (traditional powder metallurgy and composite materials). An alternative is to create a composite of cast metal pieces by super-deep penetration (SDP). Super-deep penetration is a complex physical phenomenon, when in a split second bunch of powder particles with a fraction less than 200 microns, accelerated to speeds of 700-3000 m/s, penetrates into the solid metal body at depth in tens, hundreds mm. An anisotropic composite is forming [1-2].

EXPERIMENTAL METHODS

For processing in SDP mode Pb and SiC powders with fraction 1-100 microns were used. The samples preparation technique includes cutting, polishing and etching in 4% nitric acid. Structures were studied by Hitachi s-4800 SEM, elemental analysis was made with QUANTAX EDS (P/B ZAF method). Electrochemical phase analysis, measurements of electrical resistance of the processed materials were carried out.

RESULTS AND DISCUSSION

Weight loss and therefore change of corrosion resistance of Al-12%Si alloy samples processed in SDP mode by Pb powder and SiC powder differ considerably at various stages. For example, the initial Al-12%Si sample after 980 minutes of electrochemical etching lost $3537 \cdot 10^{-8}$ kg, sample processed with Pb powder lost $2578 \cdot 10^{-8}$ kg. Thus its corrosion resistance increased compared to the initial material by 18%. At that time the Al-12%Si sample processed by SiC powder lost $4211 \cdot 10^{-8}$ kg, i.e. corrosion resistance of SiC powder processed material decreased by 27%.

The measurement of the electric resistance revealed an increase in electrical resistance in the longitudinal direction by 1.5 times. Thus material with high anisotropy of electrical properties was created.

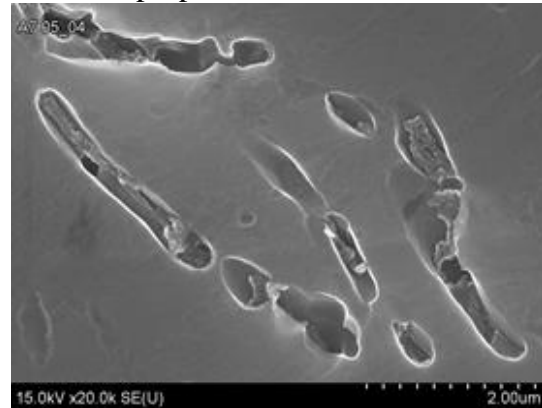


Fig.1. Structure of sample processed by SiC powder in SDP mode

CONCLUSION

Depending on the composition of powders and matrix material it is possible to vary properties of the resulting composite in a wide range. Thus, processing by Pb powder allows creating corrosion-resistant materials, and processing by SiC powder - porous filter material.

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New Composite Materials Based On Intermetallics for Protection Details of Hydropower Equipment from Cavitation, Hydroabrasive and Corrosion Wear

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INTRODUCTION

The development of new composite materials and coatings based on intermetallics is advanced direction of modern material science. The special attention is given to powder materials for plating protective coatings, especially by intermetallic NiAl and NiTi. However, the development of composites based on Ni-Al and Ni-Ti systems with the addition of refractory compounds such as carbides, borides of titanium, tungsten and zirconium and so on, which should have high wear- and corrosion resistance is an actual. Creating new and improving existing materials is currently one of the priorities for the development of shipbuilding – for protection against corrosion in water medium, as well as hydropower sector – to protect the equipment from hydro-abrasive wear and cavitation [1-3]. Therefore, the research of corrosion and cavitation behavior of materials in natural corrosive environment has considerable interest. The aim of work is development of new composite materials with high corrosion and cavitation resistance for protection of various units of shipbuilding industry and hydropower equipment, floating oil and gas platforms from hydro-abrasive wear, as well as from aggressive action of water medium including seawater.

EXPERIMENTAL METHODS

The objects to be studied were composite materials NiAl-CrB₂ and NiTi-CrB₂ systems. The laboratory tests of developed composite materials in 3% aqueous solution of NaCl, simulating sea water, as well as comprehensive researches of materials on cavitation and hydro-abrasive resistance have been conducted.

The microstructure and chemical composition of developed composites were determined using a JEOL JAMP-9500F microanalyzer.

RESULTS AND DISCUSSION

The peculiarities of phase and structure formation of composite materials based on intermetallic NiAl and NiTi with the addition of refractory compounds have been researched, the optimal composition and ratio of structural components of composite materials have been determined. The new composites and coatings with increased operational characteristics have been created as a result of research, namely: composites of NiAl (NiTi) -Ti (Cr, Zr) B₂ system with different content of refractory phase (15-45 wt.%) for increasing corrosion and cavitation resistance of various structures in aggressive water medium, including seawater.

CONCLUSION

In this paper shown that the ability to increase the reliability and operational life of the components of shipbuilding and hydropower equipment in general is given due to development of new composite materials and coatings.

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Modification of Porous Cordierite Ceramic

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INTRODUCTION

The main property of cordierite ceramic is the low thermal expansion coefficient, which determines the most important use of this material [1]. In the present work porous cordierite ceramic is produced with method where pore formation is concerned with elimination of hydrogen in result of chemical reaction between aluminum and water in the concentrated suspension [2]. The aim of work is modification of some properties of cordierite ceramic such as pore structure, thermal conductivity and mechanical strength.

EXPERIMENTAL METHODS

Cordierite ceramic was produced by using of following raw materials: talcum, γ -alumina, kaolinite and aluminum paste. Oxides used as additives were silica and non-stabilized zirconia in amount 5 wt%. Pore formation was occurred during solidification process of suspension. Sintering temperature was in the range 1250-1450 °C. Sintered samples were characterized by mercury porosimetry, phase composition by XRD, SEM. Following properties were determined: thermal conductivity depending on the temperature by Laser Flash impulse method, thermal expansion by horizontal dilatometer and compressive strength.

RESULTS AND DISCUSSION

Porosity of all synthesized samples was above 60% and depends on the sintering temperature as well as type of additives. Additive of silica decreases porosity, but additive of zirconia increases porosity at the some sintering temperature. XRD analysis shows presence of cordierite in the samples sintered at temperatures 1250-1400 °C. Thermal conductivity of sintered samples without and with additives in the test range from room temperature until 600 °C changes slightly and was in the range 0.20-0.25 W/m.K. Some increasing of coefficient of thermal conductivity take place over this

temperature and reaches 0.8-1.2 W/m.K for samples produced without additives of silica and zirconia.

Structure of materials depends also on the sintering temperature. Structure of materials was more homogenous by rising of sintering temperature (Fig.1.).

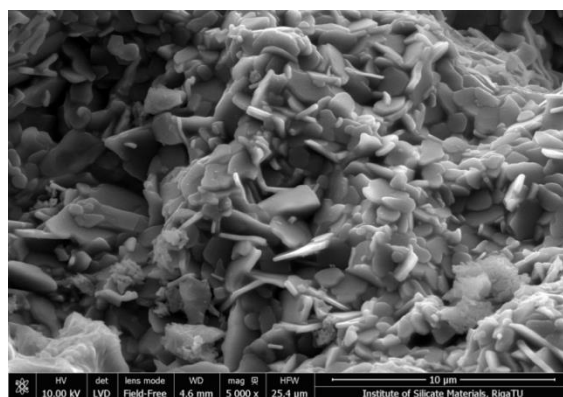


Fig.1. Porous cordierite ceramic without additive sintered at temperature 1300 °C

CONCLUSION

Additives of silica and zirconia decreases thermal conductivity of cordierite ceramic. Additive of silica decreases but additive of zirconia decreases porosity of ceramic. Compressive strength in the both cases increases.

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Biomaterials research and development from bench to bedside at Rudolfs Cimdins Riga Biomaterials Innovations and Development Centre of Riga Technical University

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Rudolfs Cimdins Riga Biomaterials Innovations and Development Centre (RBIDC) is a part of Riga Technical University (Latvia). The RBIDC research team is composed of chemists, chemical engineers and materials scientists.



Currently at RBIDC scientists are working on well-defined research areas for bone tissue replacement and regeneration. Materials such as calcium phosphate ceramics and bone cements as well as phosphate glasses and glass-ceramics are historically developed research areas in RBIDC for more than 15 years. Biomaterials developed at RBIDC have been tested in clinical practice with more than 400 patient cases in cooperation with clinicians from Riga Stradins University (Latvia).

Additional research fields include hybrid biomaterials, such as, calcium phosphate and polymer composites, microencapsulation of biologically active substances, bimodal porous calcium phosphate bioceramic scaffolds for controlled drug delivery and nanostructured

implant composites with drug eluting properties.

Currently research team includes 15 early stage researchers and PhD students with background in chemistry, chemical engineering and materials science. The team has experience in several local and international projects, like ERDF, EURONANOMED and ERA-NET projects, where the cooperation with international scientific and industrial partners occurs. In last 5 years scientific results have been presented in more than 70 scientific papers indexed in Scopus and are covered under 7 national and international patents.

RBIDC have built a successful network of partners abroad and collaborates with higher education bodies and research centers in Germany, Switzerland, Finland, France, Argentina, Italy, United States of America, Poland, Lithuania and Estonia. RBIDC takes part in three national research projects and four international research projects, as well as in the establishment of National Importance Research Centre.



Cross-linked dexamethasone sodium phosphate delivery systems based on silver doped hydroxyapatite scaffolds

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INTRODUCTION

Hydroxyapatite (HAp) possess high bioactivity and osteoconductivity, therefore it can create strong bonds with the healthy bone tissues [1]. By adding antibacterial effect with silver ions to the HAp properties and creating controlled dexamethasone sodium phosphate (DEXA) delivery systems, multifunctional material could be obtained. Such material would combine not only the properties of HAp and silver, but at the same time would release controlled amount of dexamethasone in post-surgery period, thus reducing the swelling as well as stimulating the differentiation of bone marrow cells [2, 3].

EXPERIMENTAL METHODS

Silver doped hydroxyapatite (HAp/Ag) was synthesized by two different wet precipitation methods: 1) A method from CaO, H₃PO₄, AgNO₃; 2) B method from Ca(NO₃)₂, (NH₄)₂HPO₄, NH₄OH, AgNO₃. Synthesized HAp/Ag composites contain up to 1wt% of silver. HAp/Ag powder was used for the preparation of dense and porous scaffolds with *in situ* foaming method [4]. Scaffolds were vacuum impregnated and isostatically pressed in 4wt% chitosan 5% acetic acid water solution, dried at room temperature and then vacuum impregnated and isostatically pressed in DEXA/DMF solution with N,N-diisopropylethylamine as catalyst for cross-linking. Morphology of scaffolds was evaluated using SEM, drug release kinetics in simulated body fluid (SBF) was determined with ultra high performance liquid chromatography method. Fourier transform infrared spectroscopy (FTIR) was used to evaluate the drug/scaffold/polymer interaction.

RESULTS AND DISCUSSION

Conjugation of chitosan C=O and C=C links with DEXA C=O links was confirmed with FTIR analysis for HAp and HAp/Ag A method

modified scaffolds. In the case of HAp/Ag B method scaffolds additional absorption band was not observed, suggesting that DEXA has not linked to the chitosan coating. The presence of silver ions affects the cross-linking between DEXA and chitosan; therefore DEXA was released faster from both dense and porous HAp/Ag B method scaffolds.

If the porous HAp and HAp/Ag scaffolds are modified with chitosan and DEXA, it is possible to delay the DEXA release from A method HAp/Ag scaffolds up to 40 h, from HAp scaffolds up to 70 h and from B method HAp/Ag scaffolds up to 4 hours (see Fig.1.).

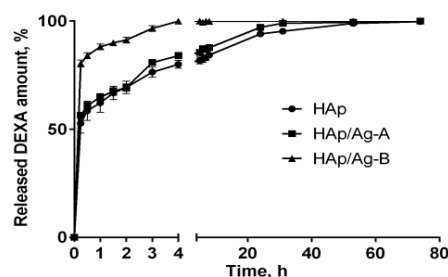


Fig.1. DEXA release kinetics from porous scaffolds

CONCLUSION

In the current research it was shown that linkage between chitosan coating and DEXA on the surface of silver doped hydroxyapatite can ensure the controlled drug release up to 70 h.

ACKNOWLEDGMENTS

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Expression Changes of *IL-1*, *IL-10*, *OPG*, *MMP2*, *BMP2/4* and *NfκB105* in Experimentally Induced Osteoporotic and Healthy Rabbit Bone

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INTRODUCTION

Bone physical and morphological characteristics are maintained by balance of bone formation and bone resorption life long. Changes of bone healing in osteoporotic patients might result in poor osteointegration and surgical failures if implants are used [1]. To overcome and facilitate bone regeneration, more and more attempts are made to develop an ideal synthetic scaffold with better biocompatibility, osteoconductivity, bioactivity, osteoinductivity and interconnected porosity [2]. Many *in vivo* and *in vitro* studies have shown that various scaffolds can accelerate bone regeneration through regulating the synthesis of different biomarkers. This is our preliminary *in vivo* pilot study to assess expression changes in osteoporotic and healthy rabbit bone of biomarkers crucial for bone homeostasis.

EXPERIMENTAL METHODS

Six female rabbits underwent experimentally induced osteoporosis by ovariectomy and followed 8 week course of methylprednisolone 1 mg/kg. Two of them had sham surgery in trochanter region with 4 mm wide non critical bone defect. Control group consisted of 4 healthy female rabbits. Investigated materials underwent hematoxylin and eosin staining protocol. Immunohistochemistry was done to evaluate expression of *IL-1*, *IL-10*, *OPG*, *MMP2*, *BMP2/4* and *NfκB105* between the groups.

RESULTS AND DISCUSSION

Expression of *OPG* was higher in control group, with less equal appearance in osteoporosis and sham surgery groups. Similarly, *NfκB105* showed more intensive rate of positive cells in control group, but less in osteoporosis and sham group. Presence of *BMP2/4* and *MMP2* was much

higher in control group, whereas twice less in osteoporosis group. Sham surgery group showed recurrence of immunoreactive structures similar to control group. Likewise, *IL-1* and *IL-10* were more superior in control group than in osteoporotic rabbits, with return of number of cells similar to control group when sham surgery was done. *IL-10* was found to be more abundant in number of structures than *IL-1* in all groups.

CONCLUSION

Constant similar decrease of *OPG* and *NfκB105* positive osteocytes in osteoporotic and sham bone represents these factors as the most stable indicators for bone regeneration. Decrease of *BMP2/4*, *MMP2*, *IL-1* and *IL-10* in osteoporotic bone with following increase in sham bone, proves the role of traumatic injury as the inducer of bone regeneration. Indistinct *IL1* with more dominating expression of *IL10* shows the correct correlation between pro- and anti-inflammatory cytokines in the osteoporotic and sham control bones.

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Change of biomechanical parameters in the lower jaws of rabbits with experimental osteoporosis after implantation of calcium – phosphate bioceramic material in the greater trochanter region

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INTRODUCTION

Osteoporosis is the most prevalent metabolic bone disease in the world involving all parts of skeleton by progressive loss of bone mass, increased bone fragility and fracture risk [1]. A number of new approaches is being explored for the prevention of fractures in osteoporotic bones [2, 3].

Objective: to define whether local use of Calcium – phosphate bioceramic material in the greater trochanter region influences on the biomechanical properties of the lower jaw at rabbits with experimental osteoporosis.

EXPERIMENTAL METHODS

Experimental osteoporosis was induced in 188 month old female rabbits by ovariectomy and following injections of methylprednisolone 1 mg/kg daily for 6 weeks. The control group consists of 4 female rabbits. On 14 animals defects in the greater trochanter region was created, 7 of which have filled with granules of a hydroxyapatite and tricalcium phosphate (HAP/TCP 30/70); 7 defects have filled with granules (HAP/TCP 30/70) together with 5% strontium ranelate. After 3 month animals were euthanased and squared samples have been cut out from a corner of the lower jaw. For investigation of biomechanical properties of the bone tissue a 3-point bending test were used.

RESULTS AND DISCUSSION

Results of research have shown that thickness of samples in control group was less, than in two other groups. The analysis

of the received results has shown that the flexure module of elasticity of a bone tissue in the control group was $5,31 \pm 1,79$ GPa, that is statistically reliable less, than the size of the flexure module of elasticity of the bone tissue in the 2nd group ($8,31 \pm 2,34$ GPa, $p=0,035$) and in the 3rd group ($7,42 \pm 1,23$ GPa, $p=0,036$), respectively.

CONCLUSION

Results of research show, that the corner of a lower jaw in rabbit becomes more rigid after filling of defects in the greater trochanter region with granules of a hydroxyapatite and tricalcium phosphate (HAP/TCP 30/70) granules together with strontium ranelate. The ultimate strain for the bone tissue in the 2nd and 3rd group is less, than for control group. Thus, local uses calcium - phosphatic bioceramic material around the greater trochanter region improves biomechanical parameters of a bone tissue in the lower jaw of animals.

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EM Shielding Properties of Metal Yarns Fabrics with Graphite Coating

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INTRODUCTION

Numerically the shielding effectiveness (SE) can be defined as relative amount of reflected and absorbed radiation at particular wavelength. Screens and shields can also be made of textile materials (woven and knitted fabrics, non-woven materials) with various structures of conductive yarns/threads, which consist of synthetic and natural fibres and as well as metals and even carbon. Several studies had been carried out about SE of fabrics where metal and metal coated yarns were incorporated into the fabrics warp and weft direction with different densities and arrangements of metal yarns [1, 2]. The goal of the study is to determine SE of fabric samples with different metal contained yarns depending on their proportional arrangement in fabric and orientation of samples relative to the radiation source of frequency 2.6-3.6 GHz, as well as the graphite coating impact on SE of these metal yarns fabrics.

EXPERIMENTAL METHODS

For fabric samples three types of partly metal yarns (A - polyester staple yarn with steel filaments; B - textured polyester multi filament yarn with steel filament; C - cotton yarn with Cu filament coated with Ag) and one multifilament polyester (PES) yarn were used in weft direction. The samples have proportionally increasing number of metal and PES weft yarns per pattern repeat (1:1, 2:2, etc.). Additionally the samples were coated with polyurethane and graphite layer (graphite particles concentration 25%).

RESULTS AND DISCUSSION

Comparing the coated and uncoated metal yarn fabric samples it is seen that layer of graphite renders the fabric samples with different pattern repeats to shield almost

equally which can be explained by the homogenous structure of the graphite coating. In general layer of graphite improves the SE properties of samples (see Fig.1.). Although, some uncoated samples have higher SE for definite frequencies than the same pattern coated samples, which requires more investigation.

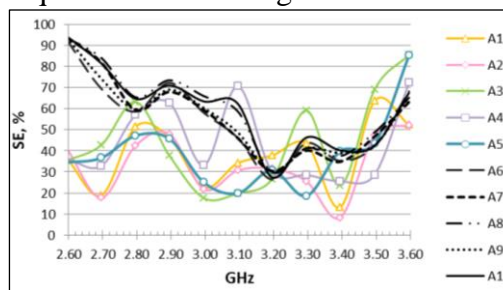


Fig.1. SE of fabric samples with yarn A, uncoated (curves A1-A5), and coated with graphite (curves A6-A10)

CONCLUSION

Graphite coating can improve shielding effectiveness (in the frequency of 2.6-3.6 GHz) of textiles with incorporated metal yarns.

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Alkaline Activated Material as a Filter Media for Wastewater with high concentration of Zinc

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INTRODUCTION

Nowadays industrial wastes are often used for developing of new materials. Previous study showed that material produced from industrial waste is applicable for removal of contaminants in different environments [1]. The production of tested geopolymer, which is alkaline activated material (AAM) requires mixing of post-industrial waste with naturally occurred aluminosilicate materials by using binding agent at the ambient or slightly increased temperature. The results is long lasting eco-friendly cementitious material [2]. The aim of this study was to test applicability of the AAM as filter media for removal of zinc from wastewater.

EXPERIMENTAL METHODS

AAM was tested for an ability to treat an industrial wastewater with a high concentration of zinc. Briefly water was pumped through glass columns (flow=5 ml/min) filled with AAM for 24 h period. Total contact time within the columns was 80,38 min. Experiment was repeated three times with different wastewater samples coming from a same factory.

RESULTS AND DISCUSSION

Results showed that AAM can effectively decrease the concentration of Zn in water (Fig.1.).

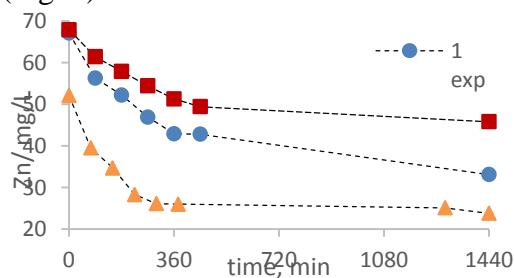


Fig.1. Concentration of Zn in water

In experiments 1 and 2 the initial concentration of Zn in water was about 68 mg/l and in 3rd-52 mg/L. The greatest decrease of Zn in water was obtained in first 75 minutes. Afterwards the decrease slows down. And after 6 hours no significant reduction of Zn was noticed. During the first 6 hours of experiments the concentration of Zn decreased by 22,27±4,98 mg/l. Taking into account that the initial concentration of Zn was high and treated wastewater was very heterogeneous and contained high concentrations of other heavy metals and organic materials (oils and esters), the result is very promising.

After the experiments the AAM was tested for structural changes using SEM and EDX methods. Used AAM was covered by thin white film, with some drop shaped inclusions. EDX analysis confirmed, that the film consists of organic substances and inclusions were made of zinc.

CONCLUSION

The study showed that developed AAM due to its alkaline can be used for removal of zinc without dosing chemicals and can be used as low cost filter media.

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ACKNOWLEDGMENTS

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Electrochemical drinking water disinfection with TiO_{2-x} ceramic electrodes at flow conditions

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INTRODUCTION

Electrochemical disinfection is regarded as one of the alternatives to chemical chlorination due to its possibility to generate free chlorine from chloride ions naturally presented in drinking water at low concentration [1].

The inactivation efficiency of electrochemical disinfection system is mostly dependent on many parameters, such as electrode material, cell configuration, electrolyte composition, microorganisms, current density and electrolyte flow rate. The choice of electrode material is one of the most important parameters which affect the efficiency of the whole process. Moreover, the overall design of the system must support simple and rapid production of disinfected water. In this study titanium oxide-based ceramic electrodes TiO_{2-x}, with a high resistance to corrosion and low absorption coefficient [2] were used to construct and demonstrate an automated disinfection system applicable for flow conditions.

EXPERIMENTAL METHODS

The electrochemical disinfection was performed in a specially made electrolytic system (EDI-001, Latvia), equipped with 24 TiO_{2-x} ceramic electrodes. *Escherichia coli* ATCC®25922 was selected as the model microorganism.

A suspension with a known concentration of *E. coli* was added to 10 L pre-filtered tap water (final concentration 10², 10³, 10⁴ *E. coli* cells mL⁻¹) and were pumped through the disinfection device (0.9 A, 25.1 V), total chlorine concentration was set at 1 mg/L Cl⁻. All experiments were performed at 500 mL/min, at room temperature (20 °C±2 °C) for 15 minutes.

RESULTS AND DISCUSSION

Contaminated tap water was completely disinfected within 15 minutes by using the

EDI-001. The results showed (Fig.1.) that during the first 5 minutes of electrochemical disinfection a more 0.24-log reduction of *E. coli* was observed which indicated on a stabilisation period. However, after further 10-15 minutes of treatment more than a 5-log decrease in cultivable *E. coli* was observed.

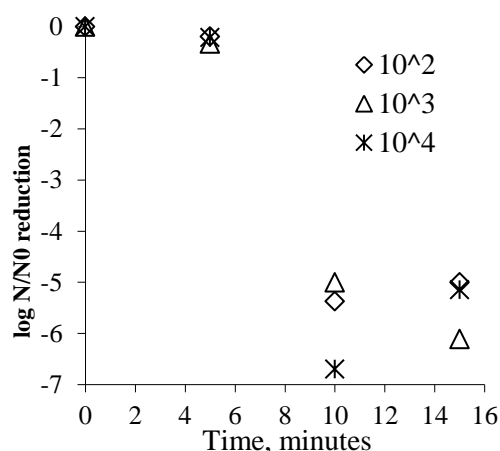


Fig.1. The effect of electrochemical disinfection (0,9A) to reduce cultivable *E. coli*

CONCLUSION

The results of the study demonstrated that the EDI-001 electrochemical device can be used as an automated disinfection system for drinking water treatment at flow conditions.

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Using STP Sludge to Produce Porous Ceramics

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INTRODUCTION

Although the EU directive and the rules for disposing of sewage treatment plant (STP) sludge and storage conditions have been adopted, it does not fully cover possible use of STP sludge for industrial purposes. Around 20000 tonnes of sludge solids are produced in Latvia per year but the strategy for an efficient use of sludge is not developed. The possible use of sludge in every country is determined by its economic status, geographic location and environmental legislation, as well as sludge quality. One of the ways of reducing amount of sludge is treatment of this waste for further application as additive or raw material for producing building materials.

EXPERIMENTAL METHODS

Clay is a mineral resource which is widely available in Latvia its quantity being one of the largest in Northern Europe. The use of porous ceramic blocks and other ceramic materials in construction is widespread in Latvia. For increasing porosity of the material different kinds of organic combustible additives (e.g. sawdust) are used.

Modern science and technology offers wide range of options to use local resources for production of various materials, therefore, despite the fact that research and development of each material is a time-consuming process, it is important to develop new materials.

Porous ceramic materials are the most sustainable materials in the market. Manufacturing of porous ceramic materials from local raw materials (e.g. clay) using water treatment sludge and sawdust as combustible filler is possible. Therefore the material with the necessary properties will be obtained, as well as new STP sludge utilization opportunities in Latvia will be created.

RESULTS AND DISCUSSION

The aim of this investigation is evaluating the possible use of sludge as organic combustible additive in manufacturing of porous ceramics.

The capacity of "Lode" Ltd., Keraterm block factory in Ane, according to company's information is 160 000 m³ of blocks per year. 0,6 m³ of clay are necessary for production of 1 m³ of blocks. Consequently, the factory needs 96 000 m³ of clay (dry weight) and 6890 t of dry sawdust per year. If the factory would produce blocks having STP sludge as 30% of the sawdust mass, then working with full capacity it could dispose around 2070 t of sludge (dry matter) per year, which is around 10% of the STP sludge produced in Latvia.

The sludge from Salaspils treatment plant storage tanks hold for more than a year, clay from the "Progress" clay mines and sawdust were used as raw materials in the present investigation.

In order to reduce the sludge humidity, freezing method was used, where sludge give away more loose water in the process of thawing.

CONCLUSION

It is concluded that the obtained ceramics has a potential strength and sustainable properties corresponding to those of Keraterm ceramic blocks.

Therefore, with the experiments it has been concluded that the wastewater treatment plant sludge can be used in the construction sector, if it is possible to process the sludge properly.

Further research is necessary to explore methods of dewatering as well as drying and calcination temperature influence on clay and STP sludge chemical indicators.

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Mechanical characterization of coatings and surfaces in the micro and nano range

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ZHN nanomechanical hardness tester

ZHN - the Universal Nanomechanical Tester - provides the force and displacement resolution necessary for comprehensive mechanical characterization of thin films and coatings or small surface areas, including measurement of indentation hardness, indentation modulus and Martens hardness to ISO 14577 (instrumented indentation hardness).

Two patents cover ZHN's measuring heads
Normal Force Unit (NFU)

Lateral Force Unit (LFU)

Working with one measuring head (Normal Force Unit), the ZHN nanoindenter functions as a depth-sensing hardness tester in the micro range, with a maximum force of 2 N. It can also be used in the nano range for indentation depths up to 200 nm. A 0.2 N head with ten times higher force resolution is optionally available.

A unique feature of the ZHN is the second independent measuring head with the same excellent resolution for the lateral direction, the Lateral Force Unit. The two measuring heads can be combined in any way required, giving a greatly increased range of measuring options. Additional uses for the machine then include micro scratch tester, micro wear tester, fatigue tester and high-resolution profilometer.

The nanomechanical tester is used as a:

- Nanoindenter
- Hardness tester
- Micro scratch tester
- Profilometer
- Fatigue tester
- Micro wear tester
- Tribometer

Investigation of mechanical properties of composite made from fibre hemp and polylactide

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INTRODUCTION

Recently, more and more popular become natural fibres and their significance in the industry increase. In addition, the product made from natural fibres can be processed several times, and finally, when it becomes unsuitable for processing, it can be easily recovered.

In this paper fibre composite consisting from hemp fibres and PLA (polylactide) binding material strength properties are investigated.

Strength properties of composite from natural fibres depend on the adhesion of fibres and matrix with each other, quantity of fibres in material, hygroscopic properties of fibres (Shahzad 2011; Ahmad *et al.* 2006, Adekunle 2015).

EXPERIMENTAL METHODS

Microstructure studies of hemp fibre composite with 15% PLA (polylactide) binder were carried out by electronic scanning microscope "JEOLJSM-7600F. Compressive strength of specimens of fibre composite was determined according to EN 826, tensile strength perpendicular to the surface - according to EN 1607, tensile strength parallel to the surface - accordance with EN 1608.

RESULTS AND DISCUSSION

The fibre composite was formed from hemp fibres and 11 to 15% PLA (polylactide) as a binder. The prepared composite was thermally treated in an oven.

In Fig. 1 microstructure of fibre composite is presented. Fibre composite structure may be described as a „three-dimensional system“ composed from many in a certain order to each other distributed and intertwined fibres.

Performed compressive stress tests have showed that at density variation of fibre

samples, consisting from hemp fibres and 11% of the PLA matrix, from $\sim 39.4 \text{ kg/m}^3$ to 97.3 kg/m^3 , compressive stress $\sigma_{10\%}$ varies from $\sim 0.25 \text{ kPa}$ to 0.42 kPa . In the case of fibre samples, consisting from hemp fibres and 15% of the PLA matrix, compressive strength tests have shown that changing the density from $\sim 44.1 \text{ kg/m}^3$ to 95.7 kg/m^3 , compressive stress $\sigma_{10\%}$ varies from 0.52 kPa to $\sim 0.51 \text{ kPa}$.

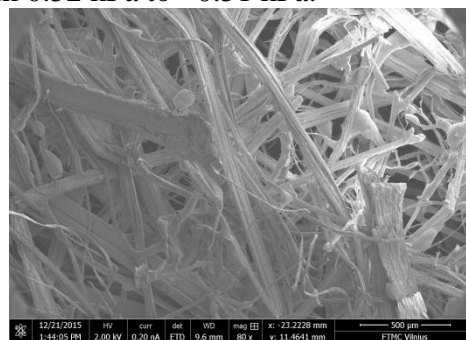


Fig.1. Microstructure of hemp fibre composite with PLA

Comparing test results of hemp fibre composite specimens with 11% and 15% of PLA binder, we have determined as follows: tensile strength perpendicular to the direction of formation increases by ~ 2.4 times; tensile strength across the direction of formation increased by ~ 1.8 times; tensile strength along the direction of formation increases by ~ 1.6 times.

Also, compressive strength of fibre composite in all directions of load application is estimated.

CONCLUSION

Compressive strength experimental data analysis has shown that it is appropriate to produce fibre hemp composite with 15% PLA matrix.

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Evaluation of thermal shock influence on cordierite ceramics using different testing methods

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INTRODUCTION

Cordierite is a mineral that is well known by its particularly low linear coefficient of thermal expansion (CTE). Theoretical cordierite single crystal expansion coefficient $\alpha = 2.1 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, but the real value of CTE is dictated by the presence of other crystalline phases as well as amorphous and gaseous phase and impurities. As a result cordierite crystal phase containing material CTE is sum of all the previously mentioned modifiers and therefore usually changes between 1.5 to $4.0 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ [1].

Most cordierite ceramic materials are used as substrate materials for filters, catalyst carriers and electronics. Pure raw materials (oxides, hydroxides) as well as kaolin and/or talc are used for production of cordierite ceramics. The synthesis temperature is usually at least $1400 \text{ }^{\circ}\text{C}$ which is close to the melting temperature of cordierite therefore a risk of defective products is always present. In order to reduce the required sintering temperature, cordierite compositions are modified with the so-called fluxes (B_2O_3 , P_2O_5 , Bi_2O_3 , etc.) which in turn deteriorate some or all of the beneficial properties of cordierite materials [2].

EXPERIMENTAL METHODS

This work explores the cordierite composite (made of clay-containing carbonates and oxides according to stoichiometric composition of cordierite) thermal shock resistance cyclic thermal shock effects. Thermal shock has been introduced using rapid water quenching technique. Different means of detection of change in modulus of elasticity have been employed in order to evaluate the impact of thermal shock including impulse extinction, three-point bending and dynamic-mechanic tests.

RESULTS AND DISCUSSION

Results have shown that cordierite ceramic thermal shock resistance, which is characterized by the modulus changes gradually decreases, the sharpest change being observed after the first thermal shock cycle (Figure 1).

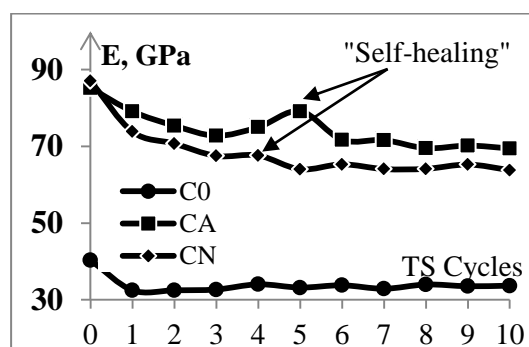


Figure 1. The change of modulus of elasticity (E) with thermal shock cycles

CONCLUSION

Cordierite materials made using clay show "self-healing" effect, which can be explained by the gradual filling of cracks with glassy phase that leads to the strengthening of the whole structure of material. This effect is directly dependent upon the composition of the sample and the material with lesser amount of glassy phase can be characterized with the largest inertia of this effect.

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Research of Laser Cladding of the Powder Materials for Die Repair

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INTRODUCTION

Laser cladding is the progressive alternative technology for the hardening and repair of the worn details of the dies, molds and machine details in comparison with conventional surface treatment [1, 2]. At that the tool steels are considered as hardly applicable for cladding due to high content of carbon and alloying elements [3]. Nevertheless some researches on the laser cladding of the tool steel are known, but the defectless coating was not achieved – the cracks were revealed [3, 4]. This work is devoted to the laser cladding of the powder materials with the object of the high stabile quality of the coating.

EXPERIMENTAL METHODS

Experimental part was carried out using industrial robot KR30HA (Kuka, Germany), cladding tool with coaxial powder supplying WT03 (Permanova Lasersystem, Sweden) and ytterbium fiber laser (IPG YRL 1000, power up to 1 kW). The powder materials (AISI: M2, A11, H13) were deposited on the different base materials: carbon steel (EN ISO 4957: C45U) and tool steel for cold working (EN ISO 4957: C80U). The influence of the overlapping of the deposited beads, as well as pre- and after heat treatment on the geometry, surface quality and tribological properties of the coating (hardness and friction coefficient) was investigated. The surface morphology was investigated with scanning electron microscope TESCAN-VEGA-LMU II (Tescan, Czech Republic). Chemical composition of samples was determined by X-ray spectrometry analysis (EDS module INCAx-act, Oxford Instruments, UK).

RESULTS AND DISCUSSION

The comprehensive investigation of the deposited beads was confirming the hypothesis about significance influence of the heat treatment on the quality of the coating in combination with the optimal parameters of cladding regime. Three different zones of the system coating-base material were examined: clad zone (CZ), interface zone (IZ) and heat-affected zone (HAZ). After the analysis of the microhardness profile it was revealed, that the microhardness decreases in following order: CZ, IZ, HAZ and base material. The deposited beads from the materials M2 and A11 have the highest microhardness values in the CZ. Besides it was established that with increasing of the overlapping of the deposited beads the coating thickness is increasing, but the weld penetration – decreasing that in turn leads to decreasing of the mixing of coating material with the base material. At minimal overlapping the maximal heat influence on the base material is revealed. In this case the HAZ is increasing and the tempering of martensite occurs – as a result, in the upper region the microhardness decreases.

CONCLUSION

High stabile quality of the coating of the tool steel during dies repair might be achieved within the optimal cladding regime and optimal ratio of the overlapping of the deposited beads as well as using heat pretreatment and after treatment of the samples. Appropriate recommendations for laser cladding of the tool steel were elaborated and offered.

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Illite Clay Ceramic Hollow Sphere - Obtaining and properties

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INTRODUCTION

Materials with custom porosity exhibit special characteristics that could be achieved by the conventional dense materials. Therefore lightweight and porous ceramic materials and structures find new application as part of technological processes as well as a final products: filters for the molten metals, support for catalysts, high temperature insulation etc. Development of new applications for the widely available natural resources and excavated (on construction sites) ground clay stimulated this research devoted to obtaining ceramic hollow sphere. Authors propose the application as lightweight substrate for the green roof, water retention agent and as lightweight filler for the construction materials [1].

EXPERIMENTAL METHODS

Clay ceramic hollow spheres (CCHS) were obtained using Devon clay from *Lode Ltd*, Latvia and expanded polystyrene (EPS) as sacrificial template at lab-scale drum granulator set-up. Obtained granules were fired at 950, 1000, 1050, 1100, 1150 °C. The compressive strength of single granule was determined by *Kahl* granule hardness tester, by utilizing 40 or more parallel tests for each sintering temperature. Water retention ability of CCHS was determined passing water through funnel filled with model soil and granules. The specific gravity and water absorption were determined by Archimedes method. Phase composition was determined by XRD using Rigaku Ultima+ diffractometer.

RESULTS AND DISCUSSION

The experimentally obtained CCHS (Fig.1.) have porosity rate of 21-36% and a water absorption rate of 15-33%. The highest rate of porosity and water absorption was

observed for hollow spheres sintered at 1050 °C.

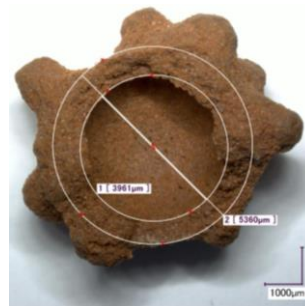


Fig.1. CCHS optical image

Increase of firing temperature led to decrease of specific surface area with the highest value at 950 °C and the lowest – at 1150 °C, the bulk density increased at 1150 °C. Mechanical strength test of ceramic hollow spheres has revealed that with the increase of firing temperature the compression strength of the spheres increases as well. Highest compression strength was observed for clay ceramic hollow spheres fired at 1150 °C. Best water retention (up to 60%) was observed samples fired at 1050 °C

CONCLUSION

Properties of the obtained clay ceramic hollow spheres make them promising material for water retention in green roofs.

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ACKNOWLEDGMENTS

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Compaction of powdered materials reinforced with milled W-B fibers

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INTRODUCTION

Fibrous composite materials such as Al-W-B, are effectively used in newest technical industries because of their high durability, small weight and other valuable properties [1]. The paper discusses methods of compaction of powder materials, reinforced by W-B fibers.

EXPERIMENTAL METHODS

For experimental studies mixtures on the base of iron, aluminum and copper powders with W-B fibers. Compaction was performed by magnetic-pulse pressing and hot isostatic pressing. Microstructure were studied with Keyence VHX-2000E digital microscope. Study of material microhardness, elastic modulus was carried out in the SCM laboratory (Peseux, Switzerland) by CSM Nano Indention Tester (NHT), tribology by CSM Tribometer (TRB). The effect of compaction and sintering parameters on the final properties of the material was established.

RESULTS AND DISCUSSION

For the preparation of mixtures were used crushed Al-W-B composite with 3-10 mm particles size and the W-B fibers, obtained after the separation of aluminum matrix by etching. Grinding of initial material was carried out in several stages: cutting of materials, grinding in a jaw crusher, double-triple grinding in disintegrator. Table 1 shows composition of aluminum based composite.

B	Al	W	Mg	Mn	Fe
47.0	43.2	5.0	2.7	1.1	0.6
5	6	6	8	6	3

Study of the microstructure showed that the samples subjected to heating to 575 °C after dynamic compaction have more uniform distribution of the structural elements in

comparison with subjected to heating to 590 °C. (Fig.1.).

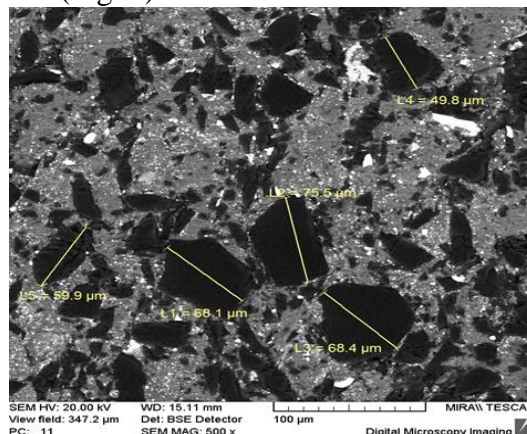


Fig.1 . Structure of Al-W-B composite samples after dynamic compaction and heating to a temperature 575 °C

CONCLUSION

Research has shown that the most technologically advanced and promising is a method of combined pressing that includes static compaction and impulse action on the material. Hot isostatic pressing of powders containing W-B fibers in aluminum ampoules allowed to reach maximal density, but its use for the manufacture is problematic.

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ACKNOWLEDGMENTS

“The authors would like to thank RTU Erasmus-Mundus IANUS II program for providing financial support to this projec

Thermal properties of lightweight alkali activated chamotte

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INTRODUCTION

Geopolymers are inorganic aluminosilicate polymers synthesized by alkali activation of Si- and Al-rich materials at near ambient temperatures [1], which are considered to be fire-resistant materials with enhanced thermal resistivity [2]. This study deals with the preparation of heat resistant (up to 1200 °C) geopolymer binders.

EXPERIMENTAL METHODS

Porous alkali activated materials were based on chamotte (S), aluminium scrap recycling waste (ASRW) as pore forming agent and leftovers from thermal ceramic bricks from stove insulation material (K26) with different proportions as heat resistant filler using 6M NaOH solution as alkali activator.

DTA/TG and DIL tests were performed for the lightweight geopolymer binders; microstructure was examined by SEM. Mineralogical composition (XRD) and chemical bonding (FTIR) of geopolymerization was characterized and physical properties were determined.

RESULTS AND DISCUSSION

Initially series of high temperature testing have been performed for samples with K26 filler from 0.1 to 1 weight parts. It has been concluded, that most promising sample with heat resistance and mechanical properties is with 50% of K26 from the mass of chamotte in the composition.

For material S-0.1-6 at the highest expanding point dimension changes draw up 0.03% at 684.4 °C degrees. Shrinkage was observed at 891.4 °C - 0.02% which corresponds to quartz polymorph transformation from α -Quartz to β -Quartz and β -Tridymite. A similar tendency was observed for other samples.

DIL curves were linked with DTA/TG tests performed; they justify phase changes in the material. It is concluded, that K26 filler limits material shrinkage. TGA results show that the biggest loss of weight occurs up to 400 °C due to dehydration for samples

without K26 filler and up to 200 °C for samples with K26. The small endoeffect stated at the temperature at 573 °C is associated with structural transition of the α -quartz SiO_2 to β -quartz.

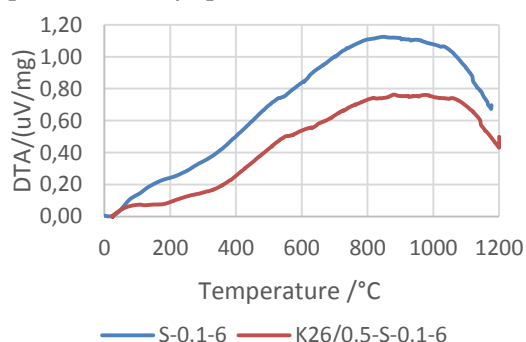


Fig.1. DTA results obtained for the materials S-0.1-6 and K26/0.5-S-0.1-6. Heating rate - 5K/min

CONCLUSION

Though K26 acts as a heat resistant ingredient it did not participate in the reaction of the initial composition of S-0.1-6.

These newly developed porous lightweight materials have a potential use in the industrial construction field as heat resistant materials as for the best composition material shrinkage at 850 °C temperature did not exceed 0.05%. For further investigation the volume change caused by quartz modification changes during heating should be considered.

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Influence of The Firing Temperature on the Illite Clay Ceramic Foam With Waste Glass Powder Addition

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INTRODUCTION

Utilization of local natural resources for production the new type of innovative material and the reuse of domestic and industrial wastes is one of the actual issues. Clay is one of the most available and cheap natural resources for the production of construction and insulation materials. The problem of waste material reuse, particularly glass, is increasing every year. In EU approximately 9 million ton of waste glass (WG) was collected in 2010. During the past decades various manufacturing methods have been investigated and developed for production of porous ceramics, such as the water-oil emulsion, replica, sacrificial template, and the direct foaming. The direct foaming is one of the fastest and easiest methods for producing of the foamed ceramics, however, number of studies devoted to the clay foam producing via direct foaming method is limited.

EXPERIMENTAL METHODS

Clay ceramic foam (CCF) with milled waste glass (soda-lime glass) was obtained using Devon clay from *Lode Ltd*, Latvia. For clay and WG effective mixing the high velocity disintegrator was used. For the clay-WG slurry obtaining high speed mixer disperser at 6000 rpm speed was used. Obtained CCF with 5, 7, and 10 wt% of WG loading were fired at 900, 950, 1000 and 1050 °C temperature. The compressive strength was determined using Universal Testing Machine (Instron: 8801), 7 parallel tests for each sintering temperature and WG content. The specific gravity and water absorption were determined by Archimedes method.

RESULTS AND DISCUSSION

The experimentally obtained CCFs have uniform pore distribution (Fig.1.), porosity rate of 65-76% and compressive strength rate of 3.8-14.3 MPa. The highest rate of porosity (76%)

was found for CCF with 10% content of WG sintered at 900 °C

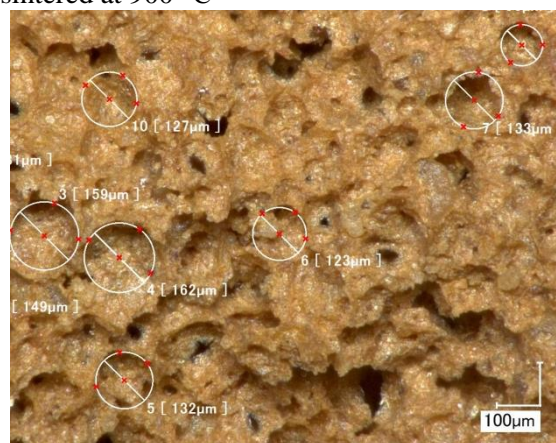


Fig.1. Optical image of CCF, with 5% of WG, sintered at 900 °C

Pores are interconnected and average window diameter is 70 µm. The WG addition had no significant influence on foam morphology and average cell sizes, which were in the 50-200 µm range for all samples sintered at same temperature.

CONCLUSION

Increase of firing temperature from 900 °C to 1050 °C lead to porosity decrease up to 6-7% for all compositions. Increase of WG addition ratio from 5 to 10 % increased porosity for 4-6%, depending on firing temperature. Compressive strength increased for all compositions, and the most pronounced results were found for compositions with 5% of WG content - 4 to 13.8 MPa.

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The properties of mineral additives obtained by collision milling in disintegrator

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INTRODUCTION

To obtain powder mineral additives often milling is used to reduce particle size distribution and morphology of obtained particles. Traditionally planetary ball milling is applied, however this method is ineffective if large quantity of material should be prepared. Grinding by collision is more effective method for refining of brittle material and one of the few machines for material grinding by collision is disintegrator [1].

EXPERIMENTAL METHODS

Semi-industrial disintegrator milling system DSL-115 with direct operating system was used for collision milling of 0/1mm natural quartz sand (QS), 0.3/2.5mm natural quartz and dolomite mixed sand (MS) and 0/4mm dolomite screenings obtained from crushing and washing dolomite rocks (DS). Two specific energy treatment regimes were applied: E_s 8.4 and 25.2 kWh/T. The particle size distribution was carried out on the vibratory sieve shaker and the laser diffraction particle sizer for fractures finer than 50 μm . The morphology (SEM) was described for obtained powder material.

RESULTS AND DISCUSSION

The particle size reduction after collision milling in disintegrator reduces the d_{10} , d_{50} and d_{90} values for all tested sand types (Table 1 and Fig.1.).

Sample	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
QS8.4	14.5	42.2	96.6
QS25.2	8.5	41.2	81.2
MS8.4	9.7	41.3	93.7
MS25.2	7.9	27.6	54.1
DS8.4	6.6	28.5	66.8
DS25.2	4.6	19.9	38.6

The increase of applied milling energy effectively reduces d_{90} value for all sand types while d_{10} size decreases significantly only

for QS. The finest particles could be obtained for dolomite sand DS – the d_{10} value could decrease to 4.6 μm .

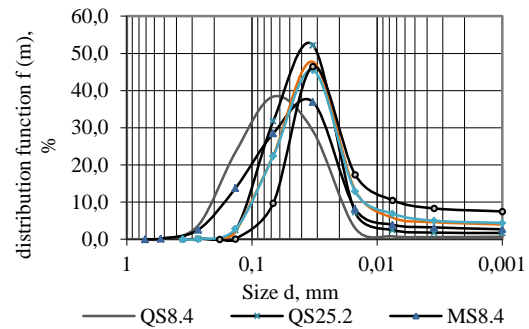


Fig.1. Particle size distribution of disintegrated sand. The morphology of QS particles has plate like structure with smooth surface while DS particles have angular shape and rough surface. The collision of particles in disintegrator splits the particle creating layered pieces. Increased of E_s reduces only the size of layered particles.

CONCLUSION

The increase of specific energy from 8.4 to 25.2 kWh/T during milling reduces the sand particle size. The d_{10} value for quartz sand reduces from 14.5 to 8.5 μm while for dolomite sand from 6.6 to 4.6 μm . Dolomite sand was milled with higher efficiency comparing with quartz sand of reducing particle size. The application of obtained material could be as microfiller in cementitious composites as fine inert mineral additive.

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Dry Sliding Tribological Behavior of Cu-Cr alloys after Equal Channel Angular Pressing

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INTRODUCTION

It is well known that the wear loss of materials during sliding depend on hardness, grain size and thermal stability [1]. The precipitation-hardened Cu-Cr energy alloys are attractive materials for electrical engineering use as they have excellent thermal and electrical conductivities. Unfortunately, these excellent properties are not studied in combination with wear resistance on sliding contacts under electrical condition.

EXPERIMENTAL METHODS

The dry sliding tribological behavior we studied by using an electrical conduction alloy-graphite sliding pair system without lubricant. The casts were forged for better dissolving of the Cr, Hf and S in Cu matrix and at follows for microstructure recrystallization were sent to heat treatment at 1000 °C for 2 h with followed cold water quenching. The ultrafine grained microstructure was produced by equal channel angular pressing for six passes by B_c route up to $\varepsilon_{VM} \approx 7.2$ of von Mises strain. For improve of the electrical conductivity, thermal stability and hardness at follows samples were heat treated at temperatures ranging from 150 °C to 750 °C for 1 h by step of 100 °C.

RESULTS AND DISCUSSION

The wear tests were conducted on experimental installation (Fig.1.).

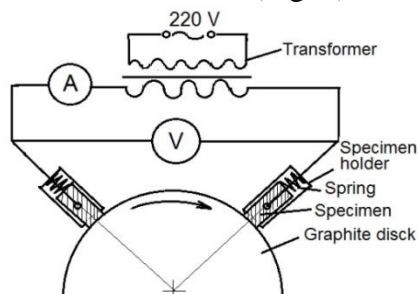


Fig.1. Schematics of the wear tester

Two samples simultaneously were tested on distance of 336 km at sliding speed of 14 km/h. The electric current density on contact surface was measured. Electrical conduction

was measured by Sigmatester 2.069 according to NPL standards. Wear tracks (Fig..) surfaces were investigated by scanning electron microscope and hardness was measured by microindentation.

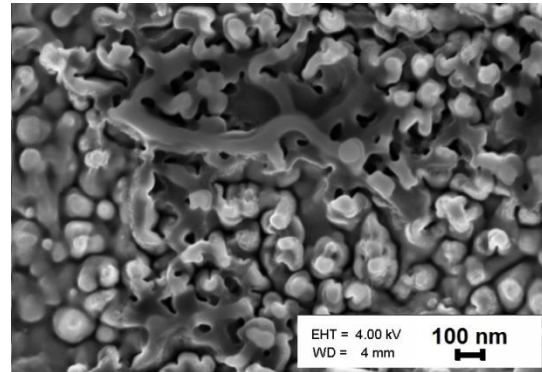


Fig.2. Wear track surface of ion milled ultrafine grained microstructure after heat treatment at 450 °C for 1h

CONCLUSION

The wear loss of CuCr alloy depends on microstructure, hardness and electrical conductivity of material as well as normal pressure stress and sliding speed. The lowest wear rates have samples after heat treatment at 450 °C for 1h.

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Tribological Properties of Nanostructured Diffusion Layers of Metal Coatings

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INTRODUCTION

Drawing covering copper-nickel on cutting tool provides decrease in temperature of its cutting edge, owing to high heat conductivity of the given covering. It will allow to raise firmness of the tool at machining [1].

EXPERIMENTAL METHODS

Researches have been executed by means of optical and electronic microscopy, the X-ray diffraction and microx-ray spectral analysis, and also carrying out tribotechnical tests.

RESULTS AND DISCUSSION

Results have shown that by means of the technology developed at the Kuban technological university and drawing copper-nickel (Cu-Ni), Fig.1, of a covering on products from tool X12M steel and the subsequent superficial plastic deformation, nanostructuring its blanket and increase in stability of operation of the tool took place.

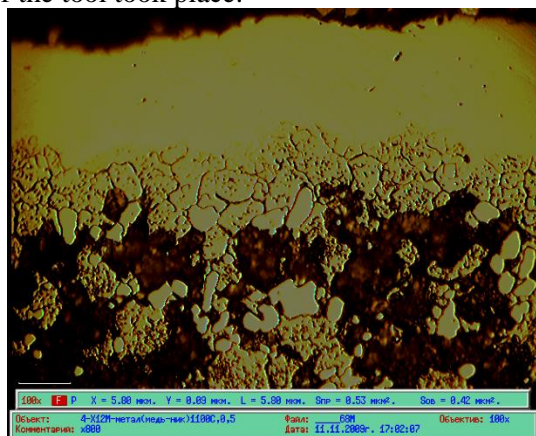


Fig.1. Structure of copper- nickel (Cu-Ni) of covering on products from tool X12M steel

After intensive superficial plastic deformation under the influence of contact pressure 4,0 ГПа, it was formed nanostructure with the size of grains 14...110 nanometers, Fig.2. Electronogram have considerably changed. "Continuous ring" an electronogram testifying to formation of supersmall structure.

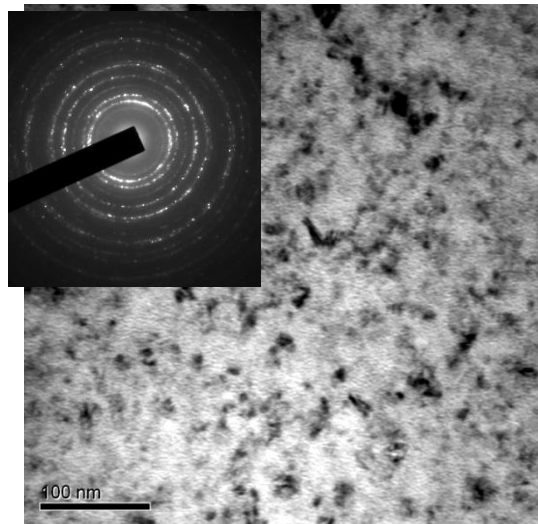


Fig.2. Structure and "continuous ring" an electronogram of metal coverings

CONCLUSION

Plastic deformation under the influence of external contact pressure from 4,0 ГПа caused reduction of internal pressure. The coefficient of friction thus decreased till 0.04, relative wear resistance of a covering to 3,53 increased.

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Influence of machining parameters on 3D surface roughness of powder slide bushings

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INTRODUCTION

In many connection units of construction machinery and transport systems are used anti-friction bushings (AB) - slide bearings. The most efficient in terms of production and operation of AB are manufactured from powder materials by powder metallurgy method [1]. Aim of the research is to study a machining of AB, and machining parameters influence of the 3D surface roughness.

EXPERIMENTAL METHODS

The paper considers machining operation (MO) of anti-friction bushings (AB) made from powder materials Fe-C-Cu used in lever brake systems of railway wagons. Following AB are designed to operate under dynamic short-term loads, providing the sliding speed up to 3 m/sec. The recommended bearings operating in the self-lubricating mode temperature is in the range of -25 to +40 °C.

For preparation of samples were used powder mixtures containing Ni and Mo less than 0.3% and with reduced phosphorous content. Research of cutting process was carried out on finished sample, which were compacted and sintered.

The cutting tool was selected so that it would provide satisfactory surface roughness of a workpiece.

RESULTS AND DISCUSSION

During the machining operation of powder parts with high porosity, such as anti-friction slide bushings, in addition to microstructure analysis, also an assessment of the product surface parameters must be performed using 3-D measurement techniques [2] (see Fig.1.) and evaluation of the morphology of the shavings must be performed (see Fig.2.).

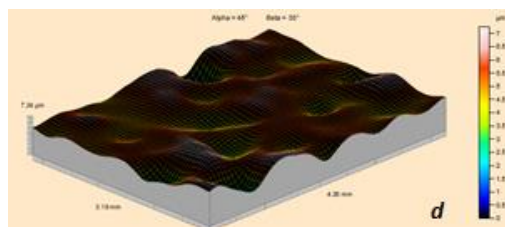


Fig.1. Waviness of the sample (Cutt-off 0,8mm)

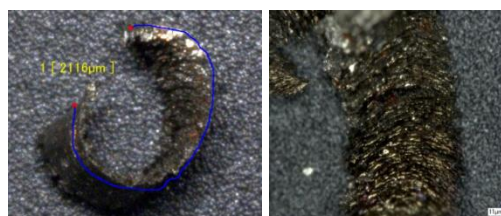


Fig.2. Morphology of the chips

CONCLUSION

When machining powder parts with high porosity, such as anti-friction slide bushings, it is necessary to select such machining parameters, which provide satisfactory 3D surface roughness. Assessment of the 3D surface parameters provide more complete picture about the machined surface. In addition to the commonly used microstructure analysis also an evaluation of the morphology of the shavings was performed.

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Welding Parameters and their Influence on the Abrasion Resistance of Structural Steels at Elevated Temperatures

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INTRODUCTION

Several industrial applications require wear and temperature resistance alloys, which can be achieved by different chemical compositions at different hardness levels. Due to harsh wear conditions at elevated temperature repair welding of components is often necessary [1]. Structural steels can provide good wear resistance and a good weldability due to their broad alloying spectrum and microstructures [2]. To understand the influence of different welding parameters on high temperature (HT) wear resistance, two different low alloyed structural steels and corresponding repair/ overlay welds with different parameters were performed, aiming to investigate the role of optimisation on the resulting microstructure and the HT abrasion resistance.

EXPERIMENTAL AND ANALYSIS

Two steels, carbon steel S355 and HT 9% Cr steel ASTM P92 were chosen for investigation. Repair welds were performed at optimised and suboptimal conditions to study the influence on wear resistance. High temperature hardness measurements were performed in a hot hardness test rig [3]; HT wear was examined within a HT continuous abrasion test up to 700 °C [4]. A detailed microstructural evaluation with light and electron microscopy of worn surfaces and cross-sections were performed to study microstructural evaluations and mechanically mixed layer formation with the abrasive and particle sticking [4].

RESULTS AND DISCUSSION

Results of both, hot hardness and wear tests are given in Fig.1. As seen in the figure, hot hardness and wear rate strongly depend on each other, but the microstructural evolution cannot be neglected, since suboptimal conditions lead to more unstable

solidification morphologies. Optimised welding parameter (according to the filler metal) lead to superior wear behaviour at all tested temperatures. Consistent microstructural properties especially at HT, are necessary for optimal sustainability.

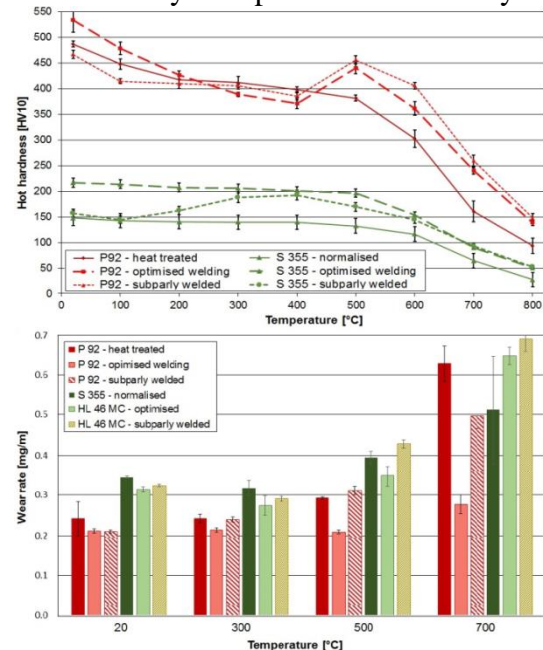


Fig.1. Hot hardness and wear rates of all materials and welding conditions tested

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Pulsed Electric Current Sintered Cr_2O_3 - rGO Composites

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INTRODUCTION

Chromium oxide is a promising material for applications where good corrosion resistance, high hardness, and high wear resistance are needed [1]. However, its use is limited because of low fracture toughness [2]. Improvement of fracture toughness of chromium oxide while maintaining its aforementioned key properties is therefore of high interest. In this communication we study the possibility of increasing the toughness of chromium oxide by the addition of graphene oxide (GO).

EXPERIMENTAL METHODS

Chromium oxide and chromium oxide - GO composite powders were consolidated applying pulsed electric current sintering (PECS) method. The GO powder was prepared by a modified Hummer's method. Additions of 0.1, 1, and 10 vol% GO were studied. In order to compare the effect of mixing two different methods were used, i.e., (i) direct chemical homogenization of Cr_2O_3 and GO powder and (ii) mechanical milling of Cr_2O_3 and GO powders in a ball mill followed by ultra sonication. Pure Cr_2O_3 and the composite powders were sintered at 1450 °C and 1200 °C, respectively, for 15 min under 50 MPa uniaxial pressure.

RESULTS AND DISCUSSION

Hardness of Cr_2O_3 was found first to increase from 18 GPa to 19 GPa and to 20.4 GPa in the presence of 0.1 and 1 vol% graphene oxide, respectively, while it decreased to 15.7 GPa with 10 vol% GO. The indentation fracture toughness was improved up to 2.5 fold with the addition of 0.1% graphene oxide. Furthermore, materials prepared by direct chemical homogenization had better fracture toughness. In composites with 10 vol% GO piling of thin graphene oxide layers resulted in the formation of graphite layers between Cr_2O_3 and in carbide formation, which were observed to be the main reasons for the

degradation of the mechanical properties. The distribution of graphene oxide was more homogeneous, when the GO amount was 0.1 vol% and the formation of graphitic layers were avoided due to lesser amount of GO as well as ultrasonic treatment following the ball milling.

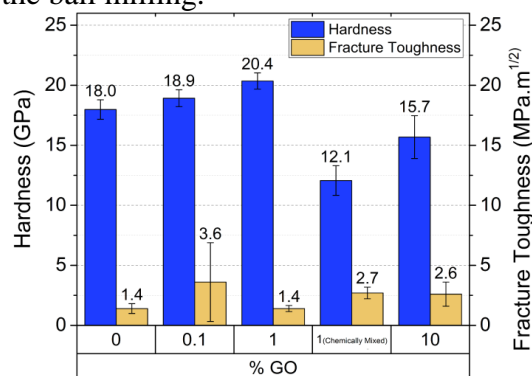


Fig.1. Hardness and fracture toughness vs. composition

CONCLUSION

The optimum GO addition to Cr_2O_3 in terms of indentation hardness is found to be very small, i.e., in the range of 0.1%. The method of mixing the GO to the composite influences the properties of the final composite. Chemical means were better for increasing toughness.

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Comparing Studies of Synthesis and Photocatalytical Properties of Various Morphology TiO₂ Nanostructures Modified With With Platinum, Gold And Silver

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INTRODUCTION

Photocatalytic activity of TiO₂ nanocatalysts strongly depends on its crystallinity, specific surface area, morphology of the particles and used dopants [1-3]. In the present work formation of active TiO₂ nanostructural photocatalysts and their modification with Pt, Au and Ag nanoparticles were studied.

EXPERIMENTAL METHODS

For TiO₂ nanostructure preparation microwave assisted [1], anodization [2] and PEO [3] methods were used. Nanofibers, nanotubes and nanopores coatings were obtained respectively. As-prepared nanostructures were modified with Pt, Au and Ag nanoparticles by using chemical deposition method and calcination at 500 °C for 2 h. Samples containing 0.1, 0.5, and 1wt% of dopant on each morphology of TiO₂ substrate were prepared. Morphology was controlled by using SEM and TEM methods. Content of dopants were controlled by XRF. Phase content was analyzed by XRD. Photocatalytical properties of 1cm² TiO₂ nanocatalyst coatings and nanofibers were determined by degradation of methylene blue (MB) solution under UV and visible light irradiation.

RESULTS AND DISCUSSION

Nanofiber layer prepared by microwave assisted method were with extra large specific surface area – 150 m²/m and with individual fiber diameter of 5 nm. Nanotubes coating on titania prepared by anodization were with tube diameter in range of 30-80 nm, but TiO₂ nanopores coating obtained on titania prepared by PEO method consisted of pores with diameter in range of 90-500 nm (Fig.1.).

Calcination at 500 °C for 2h allowed to obtain anatase.

Modified TiO₂ catalysts were with higher photocatalytical activity under UV

illumination with respect to pure TiO₂ nanostructures. The highest photocatalytical activity showed nanofiber sample containing 1% Au. Activity of catalyst depending on dopant increased in the following order: Ag<Pt<Au. By increasing the amount of dopant activity of prepared photocatalyst increases. Each of obtained photocatalyst ensured degradation degree of 95% of MB under UV irradiation, but the duration of illumination time differed. Nanofiber samples reached MB degradation degree of 95% in about 3x shorter time than nanotube and nanopore coatings samples. Under visible light irradiation the highest activity showed nanofiber sample with Au content 1%. Degradation degree of MB reached 14.6% of degraded.

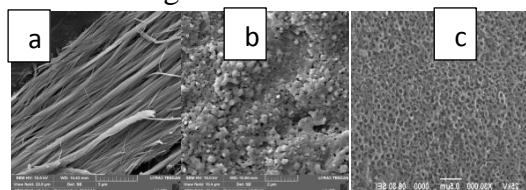


Fig.1. SEM micrographs of TiO₂: a) nanofibers (5 µm bar); b) nanopores (2 µm bar); c) nanotubes (0.5 µm bar)

CONCLUSION

Modified TiO₂ photocatalysts are with up to 50% higher activity with respect to pure TiO₂ anatase powder. Catalysts modified with Au had higher activity with respect to that of modified with Pt and Ag. Catalysts with nanofiber morphology are with up to 3x higher photocatalytical activity.

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Evaluation of Residual Stresses in Al-based PVD Coatings by Means of Curvature Method of Plate

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INTRODUCTION

Physical Vapor Deposition (PVD) coatings are designed primarily for metal cutting tools that operate in extreme machining and blanking conditions. Residual stresses arising during coating deposition have a significant effect on the service life of the coating through influencing mechanical and tribological properties and adhesion [1, 2]. The aluminum based hard coatings AlTiN, AlTiSiN (nanocomposite, commercially known as nACo), AlCrN, and AlCrSiN (nanocomposite, commercially known as nACRo) were investigated. The selected coatings have high wear and oxidation resistance, owing to the formation of protective aluminum and chromium oxide surface layers, and good thermal stability; also they are the most interesting coatings in the field of metal cutting tools [3, 4]. Residual stresses in the mentioned coatings on a TiN or CrN adhesion layer are determined, where a steel or nickel steel plate served as the substrate.

EXPERIMENTAL METHODS

The obtained mean residual stresses in the coatings were calculated from the deflection of the plate, where the equation is based on Stoney's formula to account for biaxial stresses [5, 6].

As the cutting edge of cutting tools placed is positioned at different angles in space, then three placement angles with respect to the cathode in the deposition chamber were used during deposition for the plates: parallel (0°), inclined (45°) and perpendicular (90°).

RESULTS AND DISCUSSION

The magnitude of residual stresses is influenced by intrinsic strain at layer growth rather than by thermal stress. The values of residual stresses were not strongly

dependent on the angle of plate placement (parallel (0°), inclined (45°) or perpendicular (90°) in the deposition chamber with respect to the PVD cathode. Initiation of micro-cracks and their propagation in the coated tool substrate can to some degree be prevented by presence of the residual compressive stress (hinders the appearance of cohesive damage) in the coating [7].

CONCLUSION

Residual stresses were compressive in range from 3.0 GPa to 7.5 GPa in all investigated coatings, and were not strongly dependent on the angle of plate placement with respect to the PVD cathode.

ACKNOWLEDGEMENTS

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Application of cyclic Vickers indentation method to investigate TiCN coating resistance to cyclic loading

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INTRODUCTION

Hard PVD coatings play an important role in increasing the wear resistance and overall life-time of industrial tools. Often the tools are operated in cyclic and alternating loads where fatigue and cracking resistance are the most important properties [1, 2].

This article investigates the single and cyclic Vickers indentation applicability towards describing the TiCN coating resistance to cyclic loading. Hardmetal substrate was used with higher (5 μm) and lower (2 μm) TiCN coating thickness. During indentation the substrate will develop radial cracks. The hypothesis is that during the cyclic indentation the radial cracks will initiate and grow in length in the substrate and will lead to subsequent coating cracking. The coating crack length growth is a measure of coating ability to withstand the cyclic loading.

EXPERIMENTAL METHODS

Hardmetal substrate WC-Co was polished to mirror finish before the deposition of the PVD coating. A servo-hydraulic dynamic mechanical testing system INSTRON 8802 and Vickers diamond pyramid indenter were used in the indentation experiments. The total indenting load was 100 N and the number of cyclic indentations per point varied from 10...10.000 indents. Radial cracks on the coatings and substrate were measured using the OmniMet image analysis software from Buehler along with the optical microscope Zeiss Axiovert 25. The TiCN coating was chemically stripped after conducting the indentations in order to measure the crack length beneath the coating (on the hardmetal substrate).

RESULTS AND DISCUSSION

The results show that the radial cracks in the substrate are longer than the corresponding cracks in the coating thus the initial hypothesis was confirmed. Furthermore the radial cracks have similar length in case of different coating thickness (Fig.1.).

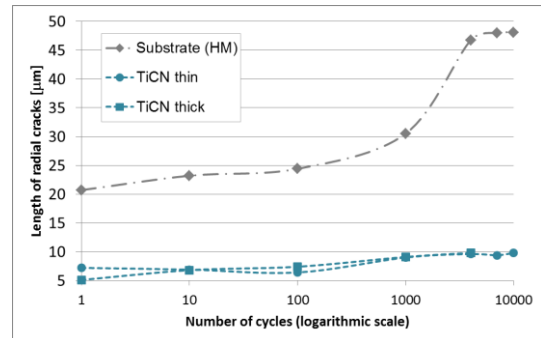


Fig.1. Radial crack length of substrate/coating

CONCLUSION

Cyclic Vickers indentation method allows investigation of cracking behavior of substrate/coating system.

The TiCN coating thickness in the range of 2...5 μm does not influence the resistance to radial cracking.

TiCN coating has high resistance to delamination during cyclic loading.

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Titanate-Based Surface Modification of Paper Waste Particles and Its Impact on Rigid Polyurethane Foam Properties

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INTRODUCTION

Concerning legislations due to environmental pollution and increasing taxes, landfills of paper waste sludge (PWS) must be eliminated. PWS particles are porous [1, 2]; therefore they can be used in polyurethane foams for thermal insulation application. Whereas the filler size, interfacial adhesion, surface characteristics and proper dispersion can greatly affect the performance of filled system [3], coupling agents may be used for the improvement not only in mechanical strength, but water absorbency and water vapour resistance as well.

EXPERIMENTAL METHODS

In order to evaluate the impact of different titanates on polyurethane foam properties, water absorbency was tested according to EN 12087 (method 2A), water vapour permeability – EN 12086, compressive and tensile strengths – EN 826 and EN 1607, respectively.

RESULTS AND DISCUSSION

Polyurethane foams were prepared with 1%, 2% and 3% of titanate coupling agents TCA-L38, TCA-L44 and TCA-K44.

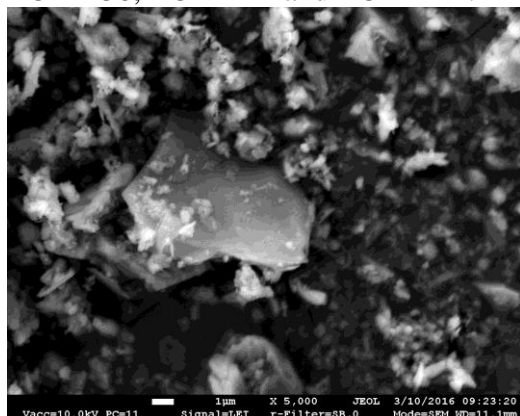


Fig.1. Untreated surface of PWS particle

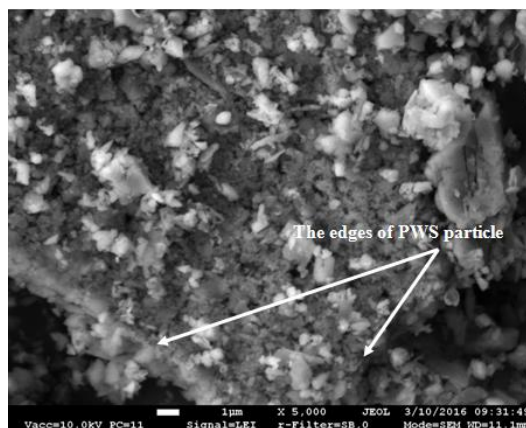


Fig.2. Treated surface of PWS particle

It can be seen from Fig.1. and Fig.2. that 3% of titanate coupling agent form a layer on the surface of particle, hereby reducing water absorption and increasing the resistance to water vapour of polyurethane foam. Mechanical properties, i.e. compressive and tensile strengths improved due to strong interfacial adhesion between particles and polymer matrix.

CONCLUSION

The results of water absorption, water vapour permeability and strengths determination show that the addition of 3% of TCA-L44 and TCA-K44 has the greatest and most favourable impact on final polyurethane foam composite properties, i.e. almost 1.5 times increased water vapour resistance and decreased water absorption. The developed foam composites were characterized by better mechanical performance.

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Fungal degradation of Wood Plastic Composites Made with Thermally Modified Wood Residues

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INTRODUCTION

Wood plastic composites (WPC) are mainly used as an outdoor material, so durability against fungal decay is one of the factors that should be analyzed and if necessary improved. WPC are susceptible to biodegradation, although these materials have limited water absorption because of the wood fiber encapsulation in polymer matrix. However in specific conditions WPCs in their outer layers can absorb more than 20-25% of moisture that is vital for fungal attacks. Fungal degradation causes substantial losses in flexural properties and influences other properties of WPCs [1]. Thermally modified wood is more durable to fungal attacks and more water resistant comparing to unmodified wood. The aim of the research was to determine, how thermally modified wood fibers influence durability of the WPC.

EXPERIMENTAL METHODS

WPCs consisted of polypropylene (50 wt%) and wood fibers (50 wt%). The fibers were obtained by crushing unmodified and thermally modified wood boards in particles that passes through 1 mm sieve. Four different types of wood fibers were used in WPC production:

- Unmodified,
- Hydrothermally modified (160°C/1h),
- Hydrothermally modified (170°C/1h),
- Hydrothermally modified (170°C/3h).

WPC samples for decay test were prepared by injection moulding (4×10×70 mm³). Two water pretreatment methods were used for these samples to ensure suitable moisture content for fungal growth.

The resistance of WPC samples to the attack by wood destroying fungi for 6 weeks was assessed according to the modified

European Prestandard ENV 12038 (2002). The specimens were exposed to the brown rot fungus *Coniophora puteana* (c.p.) and white-rot fungus *Trametes versicolor* (t.v.). Flexural properties before and after fungal degradation were determined in compliance with the standard EN ISO 178.

RESULTS AND DISCUSSION

Weight loss for WPCs with unmodified wood fibers was around 4%, however in case of thermally modified wood fibers at the same water pretreatment conditions was 1 to 3% (depending on regime). Both modulus of rupture and modulus of elasticity (MOE) decreased for all WPCs types (Fig.1.). However, WPCs with thermally modified wood fibers showed improved fungal resistance based on weight loss data and changes in flexural properties after fungal exposure.

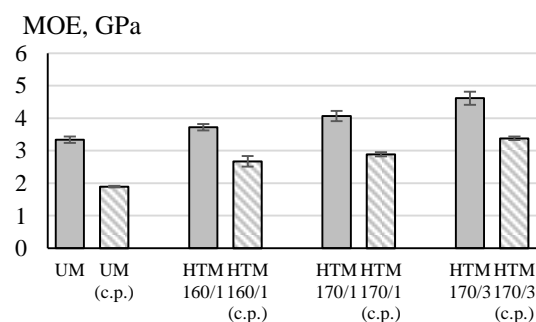


Fig.1. MOE of WPCs before and after *Coniophora puteana* (c.p.) fungal degradation

CONCLUSION

WPCs with thermally modified wood fibers are more durable against fungal degradation.

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Poly(oxyethylene) Solid Composite Electrolytes Containing Low-Content Graphene Nanoplatelets and Carbon Nanotubes

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INTRODUCTION

The main attraction of nano-composites are very high operation properties, such as flexibility, elasticity, recycling, hardness, resistance to abrasion, optical and electrical transmission and it's wide usage in different industries, such as, mechanical engineering, medicine, packaging industry, building and electronics. Polyethylene oxide (PEO) composite can be used as ion source in rechargeable batteries [1]. Polymers containing nano-sized fillers in comparison to general filled composites have shown better mechanical and physical properties due to nanoparticles tremendous surface area and high aspect ratio [2]. PEO/Lithium triflate solid composite electrolytes containing low-content graphene nanoplatelets (GR) and multi walled carbon nanotubes (MWCNT) were prepared. Effect of low-content GR and MWCNT on the electrical and thermal properties of PEO/Lithium triflate solid composite electrolyte are investigated and discussed.

EXPERIMENTAL METHODS

PEO (100000 g/mol, *Scientific Polymer Products*) composite containing Lithium triflate (LiTrifl) (*Fluorochem*), MWCNT (average D=9.5 nm, average L=1.5 μ m, *NanocylTM NC 7000*) and GR (average thickness 7.5 nm, *XGnP Sciences*) by solution casting and additional hot-pressing method were prepared. Dielectric spectroscopy (DS), volume conductivity measurements (VCM) and differential scanning calorimetry (DSC) are performed to evaluate nanoparticles of low-content on solid composite electrolytes.

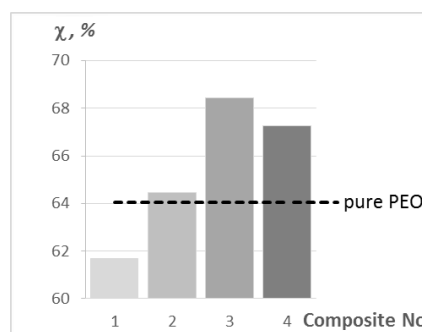
RESULTS AND DISCUSSION

The compositions of prepared PEO/LiTrifl solid composite electrolytes containing low-content GR and MWCNT are illustrated in table 1.

Table 1. shows the filler content in studied PEO composite samples

SAMPLE No	LiTrifl, wt%	MWCNT, wt%	GR, wt%
1	5	0	0
2	5	0.05	0.05
3	5	0.25	0.25
4	5	0.5	0.5

It was evaluated, that adding of low-content of GR and MWCNT increase PEO/LiTrifl solid composite electrolyte crystallinity (graph 1).



Graph 1. Crystallinity of PEO/LiTrifl solid composite electrolytes

CONCLUSION

It was concluded, that application of low-content of 0.05, 0.25, 0.5 wt% of MWCNT and GR is a proper way to control structural and conductivity properties of PEO solid composite electrolyte. Received composite electrolytes can be used as energy storage material in the production of rechargeable batteries.

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Synthesis and characterization of new poly(urethane-amide-imide) thermoplastic elastomer for fiber reinforced composite materials

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INTRODUCTION

Currently has been an increasing interest in thermoplastic elastomers, which are generally block copolymers consisting of soft and hard block. The PAIs have excellent thermal, physical and mechanical properties and may be modified by chemical synthesis[1, 2].

EXPERIMENTAL METHODS

Synthesis

For the base polymer has been chosen PAI Tarlon. In this work polymer were synthesized using these diamines: *m*-Phenylenediamine (MPD), 4,4'-oxydianiline (ODA), 4,4'-(1,1-Biphenyl-4,4'-diylidioxy)dianiline (BAPB), Bis[4-(4-aminophenoxy)phenyl] sulfone (BAPS).

Also for the synthesis of poly(propylene glycol) terminated 2,4-diisocyanate (TDI 2300), Mn=2300 and 4-Chloroformylphthalic anhydride were used.

Figure shows the way of synthesis of the polymer with MPD diamines.

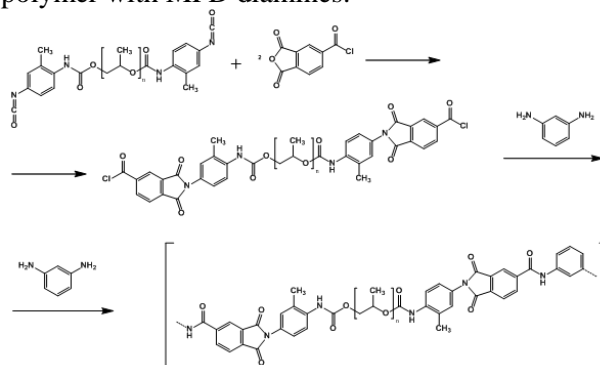


Fig.1. The scheme of polymer synthesis

Methods of analysis

The synthesized polymers were studied by DSC, TGA (NETZSCH DSC 204F1), DMA (NETZSCH DMA 242C) and nanoindentation (Hysitron TI 750) methods.

RESULTS AND DISCUSSION

DSC study showed that the T_g of polymers is in the range from -65.3 to -43.9 °C, it was also confirmed by DMA results. DMA curves verify, high elastic properties of

obtained polymers (Tab.1). TGA results indicate the onset temperature of thermal degradation of the polymer, at an average of 300 °C.

Table 1. Characteristics of the synthesized polymers

Polymer with various diamines	T_g (DSK), °C	T_g (DMA), °C	Temperature of the beginning of thermal degradation, °C
MPD	-65.3	-81	312
ODA	-51.4	-74	300
BAPB	-47.0	-66	297
BAPS	-43.9	-68	295

Polymer's nanoindentation shows that an increase of the number of benzene rings in the diamine increases the hardness and elasticity modulus of the material.

CONCLUSION

The method of synthesis of thermoplastic elastomers based on urethane groups with PAI had been suggested and it was shown the ability to adjust their mechanical properties through the introduction of various diamines. These polymers can be processed by injection molding and are promising for producing fiber reinforced composite materials.

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Curing Kinetic Models of Resins for Microwave Assisted Pultrusion Processes

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INTRODUCTION

Pultrusion process could be made more effective applying instead of conventional heaters a high frequency electromagnetic energy source. An effective set up of advanced pultrusion process is not possible without a numerical analysis of the technological process when the curing kinetic model for a matrix material should be developed separately.

EXPERIMENTAL METHODS

Experimental data of three DSC scans carried out at different heating rates 2... 10 °C/min have been used as an initial data to build the curing kinetic models of the resins. Traditional description of the rate of the thermoset resin reaction by the Arrhenius relationship multiplied by a reaction function has been used in this study. The Kissinger method [1] and ASTM E 698 procedure [2] based on the Ozawa method have been used for a determination of physical parameters of the Arrhenius relationship: activation energy and frequency factor. *N*-th order, Prout-Tompkins [3] and Kamal-Sourour [4] models have been used and evaluated as the reaction functions to formulate the curing kinetic models. The least squares method has been applied to obtain non-physical coefficients of the reaction functions by fitting the experimental heat flow curves.

RESULTS AND DISCUSSION

The proposed methodology for a building of the curing kinetic models has been successfully validated by using DSC data obtained with Netzsch DSC-204 Phenix analyser for an epoxy resin in [5]. The best precision has been obtained with the Kamal-Sourour model but the *n*-th order model gave the worst result (Fig.1.).

An engineering tool based on Microsoft Excel code has been developed by using the developed methodology. This tool has been

successfully applied for a building of the curing kinetic models of polyester, epoxy and vinyl ester resins with high microwave absorption properties to be used in the advanced pultrusion processes.

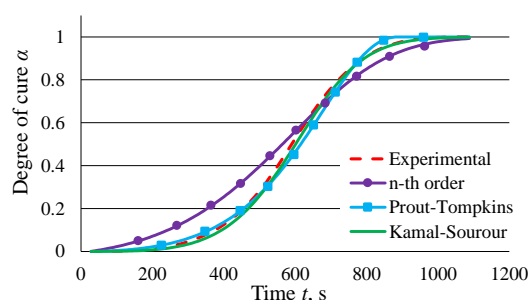


Fig.1. Dependences of the degree of cure on time for the heating rate 7.5 °C/min

CONCLUSION

The present methodology and Microsoft Excel tool has been developed and validated for a building of the curing kinetic models of different type of resins by using the results of DSC scans not dependent on data formats applied in thermo-analytical machines.

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Evaluation of Equilibrium Moisture Content and Chemical Composition in Torrefied Birch Wood

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INTRODUCTION

It is clear, to satisfy our needs for energy we can use biomass due its unique physical and chemical structure. Biomass is hygroscopic material by its nature. It may absorb and desorb the moisture from the surrounding atmosphere. Therefore, during the rainy season, the stored biomass can absorb a significant amount of moisture. For example, the equilibrium moisture content of wood at the certain temperature and relative humidity can vary from 0.1 to 24.3% [1]. The method of removing moisture from the biomass and improving its hydrophobic properties is to use torrefaction. It is a thermochemical treatment of biomass at 200 to 300 °C under atmospheric pressure and in the absence of oxygen. Despite the advantages of torrefaction, there are some disadvantages as well. One of them is that the hemicelluloses, cellulose, and lignin of biomass change its structure during the torrefaction process [2]. So, the biomass loses its mass and heating value with no appreciable change in volume, accordingly. Therefore, it is necessary to develop torrefaction process that gives the best equilibrium moisture content/heating value ratio. We tried to find out by structural carbohydrates analysis at which conditions hemicelluloses, attributed to hygroscopicity of fuel, are completely degraded.

EXPERIMENTAL METHODS

Birch wood was used as the raw material. The torrefaction process was conducted in an externally heated rotating bench-scale reactor at six different temperatures (250, 260, 270, 280, 290, and 300 °C). The time of torrefaction was constant (30 min). The evaluation of equilibrium moisture level of untreated and torrefied birch wood was studied at constant climatic conditions ($65 \pm 2\%$ relative humidity, 22.8 ± 0.3 °C). The chemical composition of fuel was

analysed according to NREL/TP-510-42618 standard method while its properties (volatiles, heating value, fixed carbon, ash content) measured according to EN standard methods.

RESULTS AND DISCUSSION

By increasing the torrefaction temperature, the properties of obtained fuel were substantially improved. Fixed carbon content reached over than 25% resulting the highest heating value 21.1 MJ/kg. Hemicellulosic compounds (defined as xylose) decreased from 20.6% in the raw material to 1.7% in obtained fuel at torrefaction temperature 300 °C, but the cellulosic compounds (defined as glucose) was degraded at lesser extent from 44.7% to 34.0%, accordingly. This lead to a lower value (up to 37.0%) of the equilibrium moisture content if we compare to the initial raw material. Results of the evaluation of initial raw and torrefied wood shavings moisture uptake also showed that the largest moisture uptake was in the first 12 hours of exposure.

CONCLUSION

Torrefaction procedure at elevated temperatures improved obtained fuel heating value and decrease the moisture absorption capacity, which was approved by changes of structural monosaccharides, fixed carbon, and volatiles content.

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Preparative Solid Phase Extraction for the Purification of Levoglucosan Obtained from Lignocellulose

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Automated preparative scale solid phase extraction (SPE) has been used to separate levoglucosan – a valuable platform chemical from the liquid products of wood pyrolysis. Up-scaling the purification of levoglucosan is a step forward industrial production of this chemical.

INTRODUCTION

Pyrolysis is a promising technology to utilize lignocellulosic biomass, such as wood wastes or industrial and agricultural residues, for renewable energy and chemicals. At optimal pre-treatment and pyrolysis conditions high yield of levoglucosan or 1,6-anhydro- β -D-glucopyranose can be obtained. Levoglucosan is a valuable platform chemical, which can be used for different products, for example, polymers functionalized with sugar moieties [1]. This work focuses on preparative SPE fractionation of wood pyrolysis as a means of purification of levoglucosan and other wood-based products. Ion exchange resins are known to be effective for the separation of normal sugars [2], so in our work ion exchangers are proposed as a sorbent for the separation of anhydrosugars.

EXPERIMENTAL METHODS

Automated preparative solid phase extraction system "Sorbomate" (Fanex, Latvia) was used for the separation experiments of pyrolysis liquids. Custom made SPE cartridges (5 cm \times 10 cm) were filled with Lewatit 1074 anion exchange resin. The resin was purchased in Cl⁻ form, but for optimal separation of levoglucosan it was conditioned with a 5% NaOH solution to obtain the OH⁻ form. The eluent was deionized water with flow rate 20 mL/min. The purity of levoglucosan was determined by iodometric titration [3]. The qualitative composition of the levoglucosan fraction was described using ultra performance liquid chromatography (UPLC) with a

Synapt G2-Si mass spectrometer (Waters, USA). The pyrolysis liquid sample was obtained at the Latvian State Institute of Wood Chemistry according to literature [4].

RESULTS AND DISCUSSION

The obtained levoglucosan fraction after SPE separation was 85% pure and could be easily crystallized. UPLC-MS showed that the levoglucosan fraction contained other anhydrosugars at smaller concentrations. The "Sorbomate" system could be used to obtain 20 g of levoglucosan from 2 L of liquid sample. Non-anhydrosugar compounds (phenols, furans *etc.*) were retained on the ion exchange resin and could be washed out with a 5% NaCl solution. Afterwards, the resin could be regenerated with NaOH and used repeatedly.

CONCLUSION

Strongly basic anion exchange resin in OH⁻ form is a suitable sorbent for the separation of levoglucosan from wood pyrolysis liquids. The method involves only aqueous solutions and can be easily scaled-up for producing large amounts of levoglucosan.

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Hydrothermal Synthesis of SnO₂ Structures with Various Morphologies in the Presence of Different Alcoholic Co-Solvents

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INTRODUCTION

While ethanol is the most common co-solvent used for the synthesis of various SnO₂ nano/microstructures by hydro/solvothermal process, it is not clear how the use of some other alcoholic co-solvents (for example, methanol or isopropanol) affect morphology and properties of SnO₂, especially if synthesis is done under similar conditions as in the case of ethanol co-solvent. In the present study, we investigated how the use of various alcoholic co-solvents (methanol, ethanol, 2-propanol, ethylene glycol and glycerol) affects crystal structure, morphology and specific surface area of the hydrothermally synthesized SnO₂. Additionally, gas sensitivity towards 100 ppm ethanol of the synthesized materials was tested.

EXPERIMENTAL METHODS

1g of SnCl₄·5H₂O and 1g of NaOH was added to 30 ml/30 ml of water/co-solvent mixture under vigorous stirring. If co-solvent was not used, the synthesis was done in a 60 ml of water. The resulting solutions were transferred into a 100 ml PTFE lined stainless steel autoclave. The autoclave was then sealed and placed inside a laboratory drying oven, heated to 200 °C, kept for 12h and afterwards cooled to the room temperature. The obtained precipitates were then collected by centrifugation, washed several times with deionized water and ethanol and dried at 80 °C for 24h. The synthesized materials were characterized by XRD, SEM, BET techniques. Additionally, gas sensitivity towards 100 ppm ethanol of the synthesized materials was tested.

RESULTS AND DISCUSSION

It was observed that the use of the respective co-solvents greatly affect morphological evolution of SnO₂ during the synthesis. The formation of nanoparticles, rod-cluster structures and spherical SnO₂ structures were observed

depending on the alcoholic co-solvent used. The synthesized SnO₂ structures show different gas sensitivities towards 100 ppm ethanol. The highest sensitivity of ~22 at 250 °C show the sample synthesized in the presence of ethanol co-solvent.

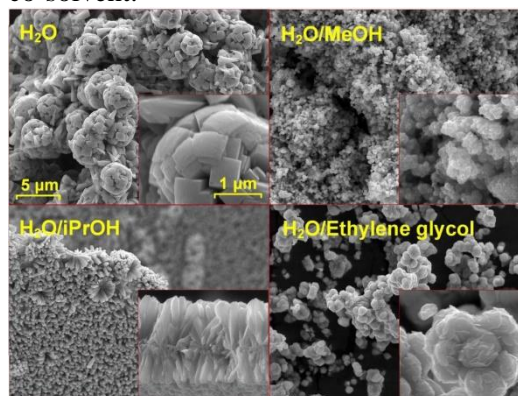


Fig.1. SEM micrographs of the hydrothermally synthesized SnO₂ structures depending on the synthesis media used

CONCLUSION

All of the examined alcoholic co-solvents greatly affect morphological evolution of SnO₂ under the synthesis conditions used. The formation of nanoparticles, rod-cluster structures and spherical SnO₂ structures were observed depending on the alcoholic co-solvent used. The highest sensitivity (~22 at 250 °C) showed the material that was synthesized in the presence of ethanol co-solvent.

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Sr- and/or Mg- Containing Nanocrystalline Hydroxyapatite: Study from Synthesis to Calcined Products

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INTRODUCTION

Hydroxyapatite (HAp) is one of the most studied biomaterials due to its similarity to the bone mineral phase [1]. Previous studies have proved enhanced osteoconductivity if synthetic HAp biomaterials chemically and morphologically resemble calcified bone tissues [2]. In the current research, an effect of addition of biologically active elements, *i.e.* Mg and Sr, on HAp crystalline structure and thermal behavior has been assessed.

EXPERIMENTAL METHODS

HAp powders were synthesized by wet precipitation method within the temperature range of 0 °C–5 °C, keeping $(Ca + Sr/Mg)/P$ molar ratio constant at 1.67 and Sr and/or Mg content up to 3.5 wt%. Final products were characterized in terms of phase, molecular and chemical composition, morphology and thermal behavior.

RESULTS AND DISCUSSION

The main characteristics of the synthesized powders are summarized in Table 1.

TABLE 1

Sample designation	Content of substituting element, wt%		Specific surface area, m ² /g
	Sr	Mg	
HAp	0.015 ± 0.002	0.166 ± 0.020	150 ± 20
Sr-HAp	3.600 ± 0.400	-	89 ± 7
Mg-HAp	-	2.800 ± 0.300	100 ± 9

SEM images showed that the as-synthesized powders have nanosized spherical-like crystallite morphology. XRD (Fig.1.) indicated that addition of Sr and/or Mg leads to the destabilization of HAp phase.

CONCLUSION

Crystallization and thermal stability of nanocrystalline HAp are significantly suppressed by addition of Sr and/or Mg into the synthesis mixture.

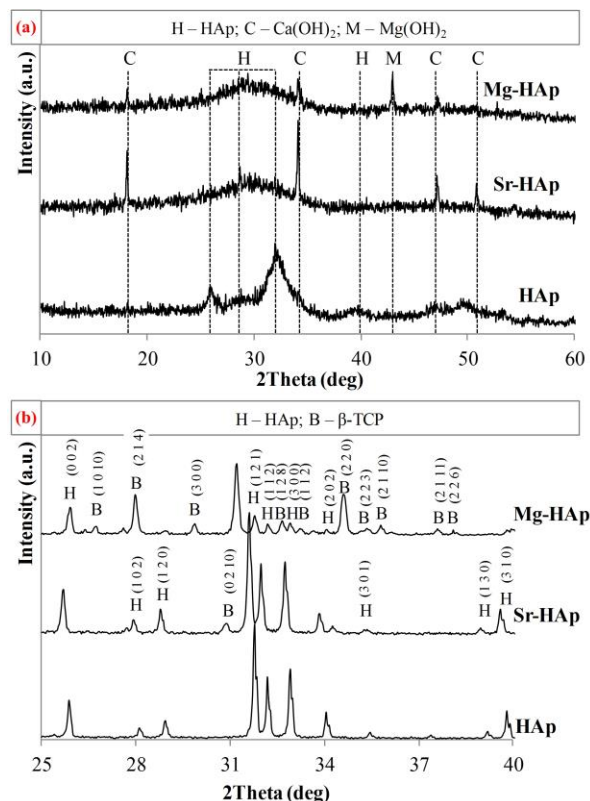


Fig.1. XRD patterns of the syntheses products: (a) as-synthesized; (b) calcined at 1100 °C (1 h)

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Effects of Calcium and Alginate Concentration on the Calcium-Deficient Hydroxyapatite Hydrogel Bead Formation

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INTRODUCTION

Natural gel-forming polymers represent an important class of biomaterials for immobilization applications. Among this class of polymers, alginate exhibits ability to undergo ionotropic gelation with bivalent ions, i.e., Ca^{2+} , Mg^{2+} , Zn^{2+} [1]. Alginate is a collective term for a family of copolymers containing 1,4-linked β -D-mannuronic and α -L-guluronic acid residues in varying proportions and sequential arrangements [2]. Alginate has been used for immobilization of various substances such as enzymes, food ingredients, proteins, drugs etc. This research project is focused on immobilization of calcium deficient hydroxyapatite (CDHAp) into Ca-alginate hydrogel and investigation of influence of $[\text{Ca}^{2+}]$ and alginate ions on the bead formation process.

EXPERIMENTAL METHODS

CDHAp/Na-alginate (%w/w) suspensions 15/1.5(A), 7.5/0.75(B), 5.0/0.5(C) were prepared according to the method [3]. 0.5 M $\text{Ca}(\text{NO}_3)_2$ aqueous (aq) and ethanolic (EtOH, 96.2% v/v) solutions each were prepared and diluted further to obtain a range of $[\text{Ca}^{2+}]$ solutions. Suspensions A, B and C were added dropwise to $\text{Ca}^{2+}_{(\text{aq})}$ and $\text{Ca}^{2+}_{(\text{EtOH})}$ solutions, using a syringe and a needle (Fig.1.).

RESULTS AND DISCUSSION

The experiment was conducted with an aim to demonstrate how the concentration affected the shape of the CDHAp beads. Gelation of the beads was modeled via proposed diffusion of Ca^{2+} through the alginate network (Eq.1) where x, alginate suspension (A) contact time with $[\text{Ca}^{2+}]$ in min and $f(x)$, hydrogel length in mm.

$$f(x) = 1.144x^{0.447} \quad (1)$$

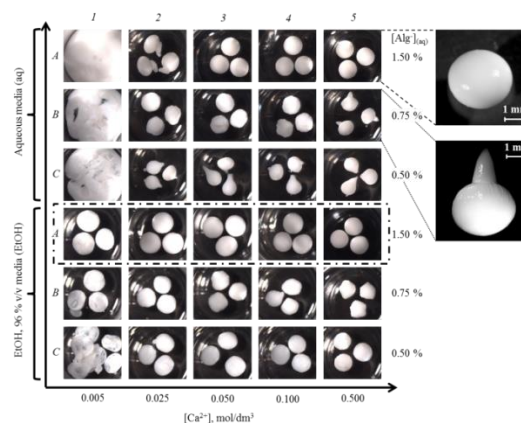


Fig.1. Top view: CDHAp/Ca-alginate beads prepared from $\text{Ca}(\text{NO}_3)_2_{(\text{aq})}$ and $\text{Ca}(\text{NO}_3)_2_{(\text{EtOH})}$ where $[\text{Ca}^{2+}]$ was 0.005, 0.025, 0.05, 0.1, 0.5 M and $[\text{Alg}]_{(\text{aq})}$ in CDHAp/ $[\text{Alg}]_{(\text{aq})}$ was 0.50, 0.75 and 1.5% w/w

CONCLUSION

The most spherical beads were obtained with composition A and 0.5 M $[\text{Ca}^{2+}]_{(\text{aq})}$. Factors affecting CDHAp/Ca-alginate bead shapes were the concentration of Na-alginate, Ca^{2+} and solvent properties. The content of CDHAp have insignificant influence on the shape. Further studies should be concluded to determine which shapes are most suited for use in biomaterials.

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Hydroxyapatite/polyvinyl alcohol composite *in situ* synthesis for hydrogel formation

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INTRODUCTION

Polyvinyl alcohol hydrogel (PVA-H) presents a remarkable resemblance to the natural articular cartilage due to the high water content and comparable microstructure [1]. Nevertheless, PVA-H lacks mechanical strength, protein adsorption ability and does not adhere biologically or chemically to the osseous tissue **thereby its** application for bone tissue engineering purposes is limited [1,2]. In order to develop a more suitable biomaterial for damaged articular repair or replacement, which is both bioactive and biocompatible, calcium phosphate ceramics - e.g., hydroxyapatite (HAp) - was incorporated into the PVA-H matrix [3] providing desirable osseointegration of the implant as well as improved mechanical properties of the hydrogel [1, 3]. In the current research HAp *in situ* synthesis in PVA solution was carried out and influence of synthesis parameters on inorganic phase chemical purity was investigated.

EXPERIMENTAL METHODS

Hydroxyapatite/polyvinyl alcohol (HAp/PVA) suspension for hydrogel formation was obtained via *in situ* wet chemical precipitation method. Starting suspension of 0.45M was fabricated by mixing PVA aqueous solution and $\text{Ca}(\text{OH})_2$ suspension. Aqueous solution of 2M H_3PO_4 was dropwise added at slow addition rate under vigorous stirring, while synthesis media temperature was maintained constant (45 °C). The quantities of reactants were selected to provide a Ca/P molar ratio of 1.67.

The content (wt%) of PVA in the final product was determined by burning out the organic phase. Phase purity of the thermally treated samples was studied via X-ray diffraction analysis (XRD). Fourier

transform infrared spectroscopy (FT-IR) was used to determine main functional groups in the HAp/PVA composite and to identify the bonds between organic and inorganic phases.

RESULTS AND DISCUSSION

Obtained results confirmed the chemical interaction between HAp and PVA. The main crystalline phase of the composite material is HAp, however phase transition $\text{HAp} \rightarrow \beta\text{-TCP}$ and undesirable by-product (e.g., CaO) formation were detected (Fig.1.).

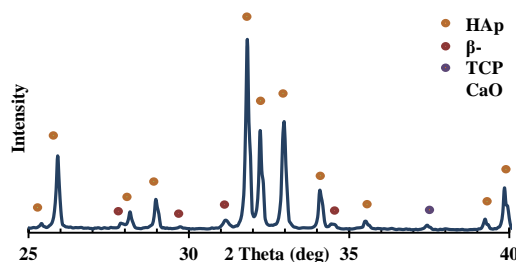


Fig.1. XRD spectra of HAp/PVA composite sintered at 1100 °C for 1h

CONCLUSION

HAp/PVA composite with weight ratio 50:50 was obtained via HAp *in situ* synthesis in the 5% PVA aqueous solution. The main inorganic phase of the composite is HAp (91.3 wt%), although small amounts of $\beta\text{-TCP}$ (8 wt%) and CaO (0.7 wt%) are also present.

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Electrophoretic Deposition of TiO₂ Nanoparticles on TiO_{2-x} Ceramic Electrodes

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INTRODUCTION

TiO₂ is one of the most widely used ceramic materials in many technological fields: biomaterials, water purification, sensors, photocatalyst *etc.* Most of applications need TiO₂ coatings or thin/thick films. Special interest is given to nanostructured TiO₂ coatings because they increase hardness, stiffness, strength as well provide antibacterial and bioactive properties [1]. Among other technologies used to produce TiO₂ coatings, the electrophoretic deposition (EPD) technique has emerged as one of the most promising technologies due to its versatility, simplicity, and low cost. EPD is based on the motion of charged particles in suspension under the influence of an electric field towards an oppositely charged electrode [2]. Our aim was to investigate the influence of EPD parameters and thermal treatment on properties of obtained TiO₂ coatings.

EXPERIMENTAL METHODS

TiO₂ nanopowder (15 nm) in anatase phase was used for EPD. The suspension was prepared by adding 0.2 g of TiO₂ to 100 ml isopropanol which contains 10ml/L triethanolamine as a dispersant and magnetically stirred for 1 h followed by ultrasonification for 5 min. Electroconductive TiO_{2-x} electrode and titanium plate were used as electrodes for EPD processes. The distance between the two electrodes was set to 1 cm. EPD experiments were carried out varying deposition time and voltage in order to determine optimal EPD parameters for high quality of TiO₂ coating on the scaffolds. The quality of the coatings was assessed by SEM and it was related to the homogeneity of the coating microstructure and to the extent of uniform covering of the scaffold surface. Deposition yield (mg/cm²) was calculated

from deposition mass and covered surface area.

RESULTS AND DISCUSSION

Fig.1. shows the cross-section and surface images of TiO₂ coating. Using low voltage and short deposition time only limited TiO₂ nanoparticles were deposited on the substrate. Optimizing deposition parameters homogeneous coating with smooth microstructure and limited surface damage can be obtained. Coatings obtained using EPD with higher voltage and longer deposition time showed microcracks and holes. Deposition yield increases linearly with increasing deposition time at constant voltage. Thermal treatment of the coating causes anatase to rutile phase transformation.

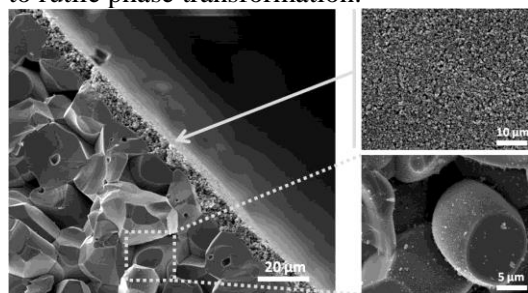


Fig.2. SEM images of TiO₂ coating obtained by EPD at 40 V for 5 min

CONCLUSION

Increasing deposition time and applied voltage, increases thickness of TiO₂ coating and in the same time decreases quality of obtained coating (cracks and holes are observed).

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Characterization and preparation of calcium phosphate model toothpaste for tooth enamel remineralization

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INTRODUCTION

Caries is the localized destruction of dental hard tissue and has been diagnosed for all age groups. The most popular and conventional solution is regular brushing of teeth with effective toothpaste, capable to supply mouth cavity with extra Ca^{2+} and PO_4^{3-} ions. Some of dentifrices and toothpastes containing hydroxyapatite (HAp) are in the market already, but there is a lack of information regarding the effective amounts that have been added to the toothpastes. Hence, the purpose of our study is to produce model toothpastes (mTP) with 5 wt%, 10wt% and 20wt% of calcium deficient HAp (CDHAp) and to observe the tooth enamel recovery.

EXPERIMENTAL METHODS

mTP was produced from 2-hydroxyethylcellulose (HOECel), glycerol and deionized water. HOECel was dissolved in the warm deionized water, then glycerol was added. After homogenisation of obtained mixture, necessary amounts of spCDHAp (spray-dried), pCDHAp (paste-like) and lyoCDHAp (lyophilized) were mixed in the HOECel-glycerine-water system. Homogenizer and sonotrode was used to destroy larger CDHAp agglomerates. The viscosity of prepared mTP was measured with rotational viscometer at 5 rpm for 10 min. The homogeneity of mTP was observed with optical microscope. 9 bovine enamel fragments were used during *in vitro* enamel remineralization (REM) for 7 days. To perform demineralization (DEM) of specimens, 35% H_3PO_4 was used. All samples were brushed with mTP twice a day for 3 minutes. The enamel blocks were stored in the artificial saliva between treatment episodes under dynamic condition at 37 °C. The surfaces of samples were

observed with scanning electron microscope (SEM).

RESULTS AND DISCUSSION

All mTP contain evenly dispersed CDHAp agglomerates in sizes less than 200 μm . The viscosity of mTP, containing 5 and 10 wt% of CDHAp, varies from 2.5 to 28.0 Pa·s. It was noticed, that viscosity is not time-dependent for pCDHAp_5%, pCDHAp_10%, spCDHAp_5%, lyoCDHAp_5%, lyoCDHAp_10% and lyoCDHAp_20%. While commercial tooth paste, spCDHAp_20% and pCDHAp_20% samples can be characterized as thixotropic suspensions. SEM revealed highly organized structure, which is built from HAp crystals arranged into bundles for DEM enamel, but formation of CaP layer was observed for enamel samples treated with lyoCDHAp_20%, spCDHAp_20% and pCDHAp_20% mTP, as morphology of surface was changed compared to demineralized surface.

CONCLUSION

Considering homogeneity and properties of viscosity, the optimal compositions of mTP were for spCDHAp_20wt%, pCDHAp_20wt% and lyoCDHAp_20wt%. *In vitro* REM study indicated new CaP layer formation on the demineralized enamel surface, but no morphological differences were found on surface for enamel samples brushed with spCDHAp_20wt%, pCDHAp_20wt% or lyoCDHAp_20wt% model toothpastes.

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Hyaluronan hydrogel/calcium phosphates composites for medical application

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INTRODUCTION

In last decade, fabrication and investigation of inorganic-organic composites based on calcium phosphates (CaP) and biocompatible polymers has attracted research interest in the field of bone tissue engineering. Mechanical properties, degradation behaviour, and cell-material interaction are among the most dominantly affected characteristics resulting from the addition of inorganic material to hydrogel networks [1]. Hyaluronic acid (HA) is a naturally derived polymer as a major component of the extracellular matrix, mediating various cellular activities, and has been widely used as tissue engineering scaffolds [2]. The aim of the current research was to obtain HA/CaP hydrogels using three-dimensional network formation in inorganic particle suspension and to investigate the influence of inorganic part on the hydrogel formation and swelling properties.

EXPERIMENTAL METHODS

A homogenous suspension of CaP particles for the preparation of HA and CaP hydrogels (HA/CaP) was obtained via wet chemical precipitation synthesis.

Hydrogels with HA concentration from 7–10 wt% were made under alkaline conditions (0.25 M NaOH), with 1,4-butanediol diglycidyl ether (BDDE) as crosslinking agent. CaP suspension was added at HA/CaP (w/w) ratios 2.33, 1 and 0.43, and mixed for 2 hours. Sol-gel transition underwent at 45 °C for 3 h, followed by sample neutralization with 0.25 M HCl. Swelling behavior of prepared hydrogels was evaluated in phosphate buffered saline (PBS) at 37 °C.

RESULTS AND DISCUSSION

The effect of HA concentration and HA/CaP ratio on the swelling behavior of the prepared hydrogels were evaluated. Swelling kinetic studies revealed that the hydrogels swelled rapidly reaching equilibrium state within 48 hours. Swelling ratio values at equilibrium state in PBS are

shown in Fig.1. Increasing polymer concentration from 7wt% to 10wt%, the swelling ratios decreased twofold, except for the sample 0.43 HA/CaP, where hydrogel failed to form with 10wt% HA.

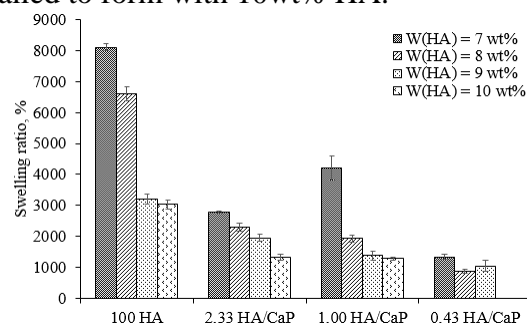


Fig.1. Swelling ratio at 37 °C in PBS

CONCLUSION

BDDE cross-linked HA/CaP hybrid hydrogels were successfully fabricated with HA/CaP ratio from 2.33–0.43. Samples were immersed in PBS solution and it was observed that HA hydrogels maintained their stable structure for 14 days and HA/CaP hydrogels for 36 days. Furthermore, the amount of CaP influenced the swelling behavior of obtained hydrogels. Addition of CaP particles to HA hydrogel reduced swelling ratio for two times.

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Precipitation Temperature Influence on Hydrothermally Treated Hydroxyapatite Nanoparticles

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INTRODUCTION

Wet chemical precipitation followed by hydrothermal treatment is commonly used method of HAp nanoparticles synthesis. Whilst hydrothermal process parameter influence on prepared HAp nanoparticles has been widely discussed [1-2], precipitation condition significance on the synthesized nanoparticles still lack some understanding. The aim of this work is to investigate different precipitation temperature influence on the afterwards hydrothermally treated HAp nanoparticles properties.

EXPERIMENTAL METHODS

Ca^{2+} and HPO_4^{2-} solutions of molar concentration 0,33 M and 0,12 M, respectively, were prepared by dissolving appropriate amounts of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and Na_2HPO_4 in deionized water. The pH of the HPO_4^{2-} solution was fixed to 11.5 by using 1 M NaOH. Then both solutions were set to specific temperature and mixed under constant stirring and maintained in constant temperature for 10 min. Afterwards suspension was transferred into a Teflon-lined stainless-steel autoclave, sealed and hydrothermally treated in 200 °C for 12 h. Suspension samples were gathered before and after hydrothermal treatment, centrifuged, washed and dried. XRD and FE-SEM methods for characterization of hydrothermally synthesized and heat treated samples (1100 °C for 1 h) were used.

RESULTS AND DISCUSSION

Obtained SEM images show obvious differences in hydrothermally treated HAp nanoparticle morphology depending on the precipitation temperature. Samples precipitated in near zero temperatures exhibit fiber-like structures, while precipitation in elevated temperatures resulted in rod-like nanostructures. XRD pattern shows low phase crystallinity HAp in precipitated samples, with significantly increasing crystallinity after hydrothermal treatment.

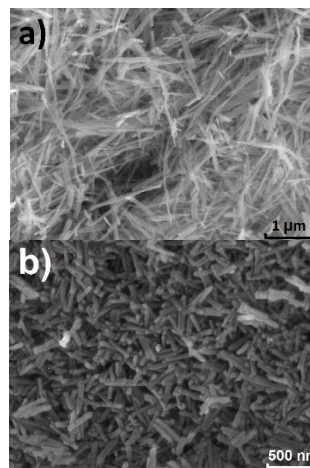


Fig.1. SEM images of hydrothermally treated HAp samples precipitated in temperature

a) 0 °C; b) 60 °C

CONCLUSION

Hydroxyapatite nanoparticles were synthesized maintaining constants hydrothermal treatment conditions, but varying precipitation process temperatures. Particles with different morphology and crystal structure were obtained, indicating that precipitation process temperature is a significant factor on hydrothermally treated HAp nanoparticles properties.

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Effect of synthesis temperature and Ca/P ratios on specific surface area of amorphous calcium phosphate

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INTRODUCTION

Calcium phosphate (CaP) materials with tuned properties are increasingly studied for biomedical applications [1]. Specific surface area (SSA) is one of the key properties that is in charge of materials solubility and reactivity [2]. This leads to improved bioactivity and ability to form new bone cause high SSA stimulates protein adsorption [3]. SSA of deprotonized bone is 87 m²/g [4], while SSA of sintered CaP is usually <1 m²/g [3]. Therefore CaP with high SSA would better mimic natural bone mineral.

The highlight of the study is systematic approach to the investigation of physico chemical properties of amorphous calcium phosphate (ACP) regarding used raw materials and synthesis conditions. Emphasis is given to SSA of obtained materials.

EXPERIMENTAL METHODS

Materials. ACP was synthesized by fast mixing of reagents: Ca(NO₃)₂·4H₂O and (NH₄)₂HPO₄. Precipitates were lyophilized for 72 h. Theoretical Ca/P molar ratios were 1.50, 1.67 or 2.2. Synthesis was done at 0 °C and 20 °C.

Methods. Obtained products were tested for their phase composition (XRD), functional groups (FT-IR), particle morphology (SEM) and specific surface area (BET).

RESULTS AND DISCUSSION

Obtained samples were x-ray amorphous regardless of varied Ca/P ratio and synthesis temperature. FT-IR spectra complemented XRD data confirming presence of ACP. Heat treatment revealed formation of β-tricalcium phosphate and α-tricalcium phosphate phases and therefore Ca/P ratio for all obtained samples was 1.5 regardless of initial Ca/P.

Average size of particles of all samples was <45 nm as measured from SEM images. Particles had spherical shape.

Higher initial Ca/P produced powders with higher SSA both at 0 °C and 20 °C. Particle formation with higher SSA could be governed by calcium ions that did not enter the expected structure with high Ca/P ratio. SSA of particles precipitated at 0 °C had smaller SSA (39, 40, 57 m²/g) than at 20 °C (53, 54, 65 m²/g). SSA values are listed with increasing initial Ca/P ratio.

CONCLUSION

SSA of obtained amorphous CaPs was affected by Ca/P ratio and synthesis temperature. In this study higher SSA was achieved at room temperature not 0 °C which is opposite to trend in the literature. Higher SSA was obtained with higher Ca/P ratio (Ca/P=2.2), unfortunately practical Ca/P was 1.5 in all cases. Therefore excess of calcium ions could have fostered formation of nanoparticles with higher SSA.

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Controllable CVD Synthesis of Graphene Layers on Copper Substrate

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INTRODUCTION

One of the basic methods of obtaining of graphene layers is the method of chemical vapor deposition (CVD). In this method volatile precursors (CH_4) decompose on a substrate surface creating a non-volatile solid (graphene). Synthesis on a copper substrate is regarded as one of the most perspective methods for obtaining graphene layers of large area.

EXPERIMENTAL METHODS

Graphene layers have been grown by CVD in a mixture of methane gas, hydrogen and argon on a substrate of copper foil (Alfa Aesar, 25 micron thickness), at a temperature of 1000 °C. The process was conducted under reduced total pressure (2.4 to 10 mbar). Polished copper substrate was annealed in a mixture of argon/hydrogen at flow rates of 250 and 15 mL/min, respectively, for reduction of the copper surface and grain growth. Then, the hydrogen flow rate was reduced to 5 mL/min, and methane was fed at a rate of 50 mL/min. Synthesis was carried out for 5-30 minutes.

In order to visualize the graphene layer copper substrate was annealed in an oxidizing atmosphere at a temperature of 200 °C. Unlike pure copper the areas covered with graphene is not oxidized, so they appear brighter as compared to the oxidized copper surface (Fig.1.).

Structural characterization of the graphene layers was carried out by micro-Raman spectroscopy. Measurements were performed at room temperature on the Horiba Jobin-Yvon T64000, equipped with a confocal microscope. X-ray photoelectron spectroscopy (XPS) was used to analyze chemical state of carbon. The measurements was performed on ThermoScientific K-alpha using an Al K-alpha X-ray source. C1s, O1s, and Cu2p data were collected to analyze thickness and a fraction of functional groups.

RESULTS AND DISCUSSION

The growth process of the graphene layer on the copper substrate is the graphene nucleation, growth and subsequent unification of the islands into a continuous layer. An increase of synthesis time does not lead to an increase in the number of layers, what is confirmed by the micro-Raman observation on the islands and the continuous layer. A typical Raman spectrum is presented in the inset to Fig.1. Using the XPS it is shown that the number of graphene layers depends on the synthesis pressure, growing from 1 to 4 when the preassure is increased from 2.4 to 10 mbar.

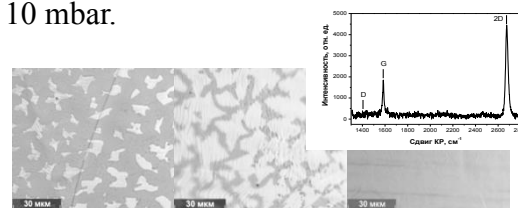


Fig.1. The microstructure of samples synthesized at a pressure of 2.4 mbar, during synthesis - 5, 10 and 15 min (a, b, c, respectively). A typical range of micro-Raman scattering (inset)

CONCLUSION

Systematic research of the graphene layers formation on the copper substrate depending on the synthesis parameters (time, preassure, etc.) is performed.

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Optimization of composition of hardmetal reinforced Fe-based PM hardfacings in abrasive wear conditions

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INTRODUCTION

WC-Co hardmetal has higher ductility than other cermets, which makes it particularly useful in hardfacings [1]. Hardfacings containing coarse hardmetal reinforcement have been found to show higher wear resistance [2]. Composite hardfacings can be produced by many means: thermal spray, cladding, casting and powder metallurgy (PM) technology [3]. Latter can be used if coarse reinforcement is needed. Previous research has focused on the influence of size [2] and content [3] of hardmetal reinforcement in the composite hardfacings on the wear resistance. This paper focuses on the morphology of the hardmetal reinforcement [4] and the influence of the shape of reinforcement on abrasive wear resistance. In our study, hardfacings with different reinforcement shapes (angular and spherical) and particle sizes (fine, coarse and twomodal) produced by powder metallurgy (PM) technology were analyzed in abrasive wear conditions.

EXPERIMENTAL METHODS

Hardfacings were produced from disintegrator milled WC-Co hardmetal scrap with cobalt binder content 12-20 wt%. Commercial Fe-based self-fluxing alloy powder (Höganäs AB, 6 AB) was used as matrix. Spherical hardmetal WC-Co reinforcement from Wansheng Cemented Carbide Ltd was used for comparison with angular reinforcement in abrasive wear tests.

Vickers macrohardness (HV30) and microhardness (HV0.3) measurements were carried out. Wear resistance was studied using ARWW test according to ASTM G 65 standard.

RESULTS AND DISCUSSION

Coarse reinforcement containing hardfacings showed better wear resistance

compared to fine and twomodal reinforcement containing hardfacings, due to cracks and high porosity in the latter. Spherical reinforcement performed better than angular.

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Comparison of Wear Mechanisms of Microcrystalline Diamond and Diamond Like Carbon Coatings Under Reciprocating Sliding and Calo-Tests Conditions

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INTRODUCTION

Diamond and diamond like carbon (DLC) coatings are the well-known wear-resistant coatings. The main goals of the present study are a comparison of the wear mechanisms of microcrystalline diamond (MCD) and DLC coatings deposited on hard metal (WC-Co) substrates and the investigation of the phenomenon of film deflection.

EXPERIMENTAL METHODS

The MCD and DLC coatings were grown using a chemical vapor deposition method (CVD). Tribological tests were carried out on the ball-on-plate type tribometer in reciprocal sliding regime with Si_3N_4 balls. The tests conditions were as following: the stroke length was 1 mm, the normal loads were 0.5 and 2N and the number of cycles was 18000, 32000 and 72000. The measurement of thickness was carried out by Calo-test. The mechanical profilometry, optical microscopy and scanning electron microscopy (SEM) were used for investigation of wear tracks after reciprocating sliding and Calo- tests.

RESULTS AND DISCUSSION

The measurements of the wear tracks depth after reciprocating sliding tests show that the wear tracks on the DLC coatings are deeper than the wear tracks on the MCD coatings. The calculation of the apparent wear volumes suggests also that the DLC coatings have a higher wear rate than that of MCD ones, see Table 1. However, the deflection of MCD coatings was found, which can furthermore reduce the wear rate values shown in Table 1 [1].

Table 1. Dependence of the wear rates on the load and number of cycles for MCD and DLC coatings

Number of cycles	Wear rate ($\frac{\text{mm}^3}{\text{N}\cdot\text{m}}$)			
	MCD		DLC	
	0.5N	2N	0.5N	2N
18000	6.2E-07	4.3E-07	2.3E-06	1.0E-06
36000	4.4E-07	2.7E-07	1.3E-06	9.8E-07
72000	2.2E-07	1.5E-07	2.2E-06	1.8E-06

The depth of the wear tracks on the DLC coatings is 3.5 μm and on MCD coatings is 0.6 μm after the Calo-tests with 400 rpm during 20 min. It means that the MCD coatings have a better wear resistance than the DLC ones, in agreement with the reciprocating sliding tests.

CONCLUSION

The DLC coatings show lower wear resistance compared to MCD ones in the reciprocating sliding and Calo- tests.

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Electrochemical behaviour of TiCN and TiAlN PVD gradient coatings prepared by lateral rotating ARC-cathodes technology

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Corrosion behaviour of physical vapour deposited (PVD) TiCN (2.2 μm) and TiAlN (3.4 μm) gradient coatings on AISI 316L was studied in 3.5 wt% NaCl solution. High protective efficiency (up to 95%) was measured for gradient coatings.

INTRODUCTION

Coatings used in aggressive environments are often affected by corrosion [1], [2]. Merl et al. [2] suggested that macro defects, such as inclusions in a dense coating, not always present a decreased corrosion resistance. Depending on microstructural defects, some hard coatings like TiN and TiAlN can protect steel leading to transpassivation in NaCl solution at too positive protected metal potential due to passive film breakdown and localized corrosion [3].

EXPERIMENTAL METHODS

The coatings of TiCN and $\text{Ti}_{0.55}\text{Al}_{0.45}\text{N}$ were deposited on a substrate by a physical vapour deposition device Platin π^{80} (Switzerland) lateral rotating ARC-cathodes technology. Obtained specimens are marked as following: uncoated AISI 316L (R), coated with TiCN (A), and TiAlN (B).

A scanning electron microscope Hitachi TM1000 was used for observation of the surface morphology. Potentiodynamic polarization measurements were performed in three-electrode cell by using Autolab PGSTAT 30 potentiostat/galvanostat.

RESULTS AND DISCUSSION

SEM images of coated samples show pinholes and macro defects. Properties measured with the help of electrochemical tests are shown in Table 1. TiCN and TiAlN

coatings show that corrosion potential (E_{corr}) shifts towards the positive side (-0.185 and -0.177 V) with down to 20 folds lower corrosion current (i_{corr}) as compared to the substrate indicating better corrosion and polarization (R_p) resistance for TiCN and TiAlN coatings over the steel substrate. Penetration rate (CR) is about 4 to 10 times lower for coated samples. Results show high protection efficiency (P_i) and low porosity (F) for obtained coatings.

Table 1. Calculated protection properties from potentiodynamic polarization data.

Sample	CR ($\text{mm}\cdot\text{year}^{-1}$)	P_i (%)	F (%)
R	$3.746\cdot 10^{-3}$	-	-
A	$8.432\cdot 10^{-4}$	89.24	0.51
B	$4.94\cdot 10^{-4}$	94.98	0.012

CONCLUSION

In present work, it was found that the selected PVD gradient coating method and obtained thickness (2.2 to 3.4 μm) ensure up to about 95% higher protective efficiency in the 3.5 wt% NaCl solution as compared to the substrate due to low porosity and high stability at short immersion time.

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Effect of Hemp Fibers Waste Pre-Processing on Linear Low Density Polyethylene Matrix Composite Properties

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INTRODUCTION

Research is focused on improving melt-flow index (MFI) and lowering water sorption of the LLDPE composites reinforced with hemp fibers and waste. Chemical modification of natural fibers waste used in this study involves mercerization treatment in order to reduce the content of hydroxyl groups and introduce cross-linking between the filler fibers and the polymeric matrix. Untreated hemp fibers composite melt with 40 wt% practically lost fluidity [1]. To improve the quality of extrusion process lubricant additive is needed.

EXPERIMENTAL METHODS

The hemp primary processing waste contains a mixture of sheaves and less valuable secondary fibers left after obtaining qualitative primary fibers. The hemp primary processing waste supplied by a Latvian company SIA "Zalers". Hemp fibers and waste pre-processing, and composite preparing method influence on MFI and water sorption are investigated. Composites with fibers content 40 wt% using LLDPE grade 6201XR as matrix and additives were prepared by rolls mill and extrusion.



Fig.1. Hemp fibers (left) and hemp waste (right)

MFI was estimated by method according to the standard ASTM D 1238-90b (T=1900 °C, P=2.16 kg).

COMPOSITE FILLER	FABRICATION METHOD	PROCESSING METHOD AND ADDITIVES
Hemp fiber	Rolls mill	-
Hemp fiber	Rolls mill	1wt% StruktoL
Hemp fiber	Rolls mill and extrusion	1wt% StruktoL
Waste	Rolls mill	-
Waste	Rolls mill	1wt% StruktoL
Waste	Rolls mill and extrusion	1wt% StruktoL
Waste	Rolls mill	2wt% NaOH
Waste	Rolls mill	1,5wt% NaOH
Waste	Rolls mill	1wt% NaOH

The following table shows the scheme of composites preparation conditions. Water exposure experiments (standard ASTM D 570-98) were carried out at a room temperature (+23 °C).

RESULTS AND DISCUSSION

Waste use as filler to compare with the hemp primary fibers reduces the composite MFI, as waste contains a lot of dust and micro-particles of grounded hemp shives. MFI of waste/LLDPE composite 0,032g/10min is very low to compare with the fiber/LLDPE composite MFI 1,46g/10min. Pre-treatment with alkali solution clears waste and reduces water sorption.

CONCLUSION

The impact of mercerization pre-treatment on the waste and hemp fiber composites properties is different. The StruktoL TPW-709 1 wt% additive does not increase the MFI as expected.

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The Nonwovens Properties Made from Hybrid Fibers

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The nonwovens (NW) made from hemp, recycled polyethylene terephthalate and polypropylene fibers were produced in two temperature and pressure conditions. The surface parameters, mechanical properties as well as air permeability and water penetration of obtained NW were tested.

INTRODUCTION

The interest in utilizing of fibers for composite materials production has been growing. Fiber-reinforced thermoplastic matrix composites have gained commercial success in the semistructural and structural applications due to the low production cycle and lower processing cost [1]. Natural fibres are relatively inexpensive and well recognised to impact good reinforcing capability to composites [2].

EXPERIMENTAL METHODS

For nonwoven web production the hemp fibers (HA; length 50-60 mm) pre-treated with sodium hydroxide (200 g/L), recycled polyethylene terephthalate fibers (PET; length 60±2 mm) and polypropylene (PP; length 20±2 mm) were used. The composition of A-A3 webs was HA- 59%, PET- 23% and PP- 18%, B-B3 webs HA- 81%, PET- 13%, PP-6%. The nonwoven web was made with laboratory carding machine (337A MESDAN) from fibers blend. Then the samples (160x160 mm) were cut out and laboratory press (LP-S-50/S ASTM) was used for nonwoven production (Table). The surface parameters were calculated according LVS EN ISO 139:2005. For testing of composite mechanical properties Zwick Universal testing machine, according LVS EN ISO 13934-1-2001 was used. For determination of resistance to water penetration hydrostatic pressure test according LVS EN 20811:2001 was applied. For air permeability EN ISO 9237:1998 was used.

RESULTS AND DISCUSSION

For nonwoven production two compositions of fibers blend were prepared; two temperatures and pressure conditions were used (Table).

SAMPLE	WEB WEIGHT, g	PRODUCTION		COMPOSITES	
		T, °C	PRES SURE MPa	THICKNESS, mm	MASS, g/m ²
A	2.57	150	32	0.38	102
A1	2.57	170	26	0.25	98
A2	3.78	150	32	0.43	136
A3	3.78	170	26	0.30	139
B	2.57	150	32	0.39	95
B1	2.57	170	26	0.28	99
B2	3.78	150	32	0.48	141
B3	3.78	170	26	0.32	143

Produced nonwovens composite average mass and thickness depends on fibers web composition, primary mass of web and composite production technology (temperature and pressure).

Higher values of tensile strength and elongation as well as water penetration are for composites with smaller hemp content produced at higher temperature conditions. The higher air permeability is for composites with smaller hemp content, produced in lower temperature conditions.

CONCLUSION

The produced NW surface and mechanical properties can be purposeful influenced with NW web composition and production technology.

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Effect of the Modification Mode of Wood Sawdust on Wettability Properties of Wood-Polymer Composite Containing It

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INTRODUCTION

Due to renewability, easy availability, low cost, biodegradability, light mass and enhanced filling degree, lignocellulosic fibres have the defined advantages compared with glass fibres as filler for composite materials. To increase the compatibility and improve the properties of wood-polymer composites (WPCs), chemical modification of wood filler is used [1]. The aim of the present study was to decrease the water wettability of wood filler by its purposeful modification and evaluate the effect of this modification on the properties of WPC based on recycled polypropylene (RPP).

EXPERIMENTAL METHODS

For modification, aspen sawdust was treated by mild acid hydrolysis and amooxidised using different amooxidation regime. The hydrolysis was performed under mild conditions (0.1% HCl, 5 h) at 60 °C and 90 °C. The ammoxidation was carried out by using ammonia persulfate and a NH₄OH solution. The content of the introduced nitrogen (N) was 1.0-2.1%. WPC samples were prepared, using a twin screw extruder and a moulding machine at 175-180 °C. Contact angle for the wood particles and the WPC samples was measured with a Kruss K100. Adhesion energy relative to water was calculated according to the Young-Dupre equation. Water sorption of the samples was determined using a desiccator's method at a humidity of 98%. Mechanical tests were made according to ASTM D638 and EN ISO 178.

RESULTS AND DISCUSSION

The WPC samples containing both the hydrolysed and amooxidised wood microparticles were characterised by enhanced advancing and receding contact angles, which did not dramatically decrease

with the growth of the filling degree, as well as by a smaller contact angle hysteresis and a lower adsorption of water vapour, in comparison with the same indexes of the WPC filled with initial sawdust. This tendency progressed with increasing hydrolysis T and introduced N. All the factors indicated a decrease in the wettability of the modified lignocellulosic microparticles towards water. This was supported by better physico-mechanical properties of the samples filled with the modified microparticles, in comparison with the properties of the WPC, containing the initial sawdust.

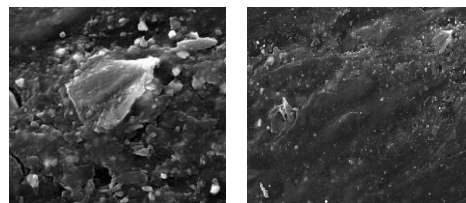


Fig.1. SEM images of WPC with unmodified (left) and modified (right) aspen wood microparticles (30% filling)

CONCLUSION

With increasing hydrolysis T and the content of the introduced N, the wettability of the modified filler towards water decreases that positively impacts the WPC properties.

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Polyurethane Binder Mechanical Properties under Different Crosslinking Conditions

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INTRODUCTION

The utilization of scrap tires still obtains a remarkable importance from the aspect of unloading the environment from non-degradable waste. One of the most perspective ways for scrap tires reuse is a production of composite materials [1]. In our previous investigations optimization of composition and technology of the composite material's production from mechanically grinded scrap tires and polyurethane type binder were realized [2]. The objective of this work is to investigate selected mechanical properties of the polyurethane type polymer binder with defined reactivity under different crosslinking conditions, taking in to consideration, that there exist close correlation between properties of the polymer binder and the obtained composite material [3].

EXPERIMENTAL METHODS

Polyurethane type polymer binder with selected reactivity (–NCO group content 2.4%) was used. Crosslinking conditions (technological parameters) of the polymer binder films were fixed as follows: T, C (18-70), relative air humidity RH,% (9-91) and hardening time, h (6-168). Shore C hardness (ISO 7619-1; ISO 868), tensile strength, elongation at break and modulus of elasticity (EN 826) were evaluated for obtained polymer binder films. DMTA (dynamic mechanic thermal analyzer) investigation of the polymer binder samples in tensile mode of loading also were realized to clear up influence of the deformation circumstances on storage and loss components of elasticity modulus of the polymer.

RESULTS AND DISCUSSION

The results show that hardening (due to crosslinking) of the polymer binder depends both on temperature and RH simultaneously. According to the experimental data relative air humidity has more principal influence on crosslinking degree of polymer than temperature. In present work influence of the

crosslinking conditions (T and RH) on tensile properties of the polymer binder were estimated. It was noted, that mechanical properties of polymer films are unessentially dependent on selected crosslinking conditions. Probably it is connected with impression of selected hardening time, leading to quite similar crosslinking degree. Therefore this must be estimated as additional affirmation, that not only temperature and relative air humidity, but also hardening time has essential impact on mechanical properties of the polymer binder.

The DMTA results show that storage modulus E, representing elastic part of polymer binder, demonstrate similar changes with variation of test temperature and is dependent on crosslinking conditions of the polymer films.

CONCLUSION

Obtained results shows some correlation between mentioned above mechanical properties and selected crosslinking conditions.

Maximum Shore C hardness values and thereby crosslinking degree of tested samples is possible to reach both at ambient and elevated temperatures, but at different hardening times and relative air humidity.

Purposeful selection and mutual combination of technological parameters can ensure quite similar crosslinking rate of the polymer binder.

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Some exploitation properties of wood plastic composites (WPC) based on polypropylene and plywood production waste

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INTRODUCTION

WPC are widely used materials in different branches of industry. In the works [1, 2] are shown that as reinforcement in polypropylene matrix successfully are able to use plywood production waste. There are found that these by-products improve physical mechanical properties of polypropylene composites if MAPP are utilized as interfacial modifier. Our research is focused on investigations of some another properties like creep deformation, microhardness and water resistance of plywood production waste containing unmodified and modified with MAPP polypropylene composites.

EXPERIMENTAL METHODS

As polymer matrix was chosen polypropylene (PP) type Mosten MA-712 (MFI=12g/10min.). Three types of waste (PSD, PSWD, RPSF) which particle length fractions characteristics are presented in [1] was used for reinforcing. As interfacial modifier served MAPP type Licocene PP-MA-7452, but thermal stabilizer Hostanox 03 P was used. Composites were prepared by rolls mill method. Samples for investigations were prepared like in [1, 2]. MFI was estimated by standard ASTM 1238-90. Creep deformation was measured in bending regime (standard ISO 899-1), microhardness was noted by Vickers M-41 at load 200 g. Water exposure experiment was carried out by standard ASTM D 570-88 at temperature +23 °C.

RESULTS AND DISCUSSION

Tensile and flexural strength measurements showed positive influence on tensile and flexural modulus of composites containing all types of by-products. The best results in the case of plywood sanding dust (PSD 40-50 wt%) was observed. Increase of tensile modulus was 6 times, but flexural modulus 2.3 times. MFI values decrease with increase of filler content till 0.6-1.11g/10min. Exception was system with 50 wt% PSD for which MFI was 0.01g/10min.

Therefore in the next experiments as optimal compound of the composites were chosen with 40 wt% PSD, 50 wt% PSWD and 50 wt% RPSF. From results of [1] for modification of these systems 5 wt% of MAPP was used. Creep deformation (CD) measurements showed increase of CD during experiment time from 0.4% till 0.8-1.2% for all composites. In the same time common tendency of increase of the values of CD in the presence of 5 wt% MAPP in composites can be observed. Water resistance investigations showed of water absorption increase with increase of water exposure time and for unmodified systems can reach 8-16%. During water uptake for all composites specimens swelling up processes are able to be observed. Linear sizes of the samples increase up to 1.5-2% for unmodified materials and 1.0-2.5% for modified with MAPP composites. It means that specimens volume under water exposure changes are insignificant. Surface microhardness examinations showed positive influence of the by-products and MAPP on microhardness of all composite materials.

CONCLUSION

Our investigations showed excellent possibilities of the usage of plywood production by-products for preparing WPC without their additional fabricating.

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Electron Beam Cross-Linking of Ethylene-Octene Copolymer Nanocomposites with Multi-Walled Carbon Nanotubes to Improve their Temperature Dependence of Mechanical and Thermosetting Properties

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INTRODUCTION

Recently, carbon nanotube fillers have found an application in radiation cross-linked thermoplastic polymers due to resonant structure of graphene layers that may prevent oxidation effects and improve mechanical properties of composites [1]. Metallocene based ethylene-octene copolymers (EOCs) have found attention in composite modification due to high cross-linking efficiency of those polymers [2]. In our previous studies we have found improvement of thermomechanical properties of nanofiller (ferrite) modified electron beam cross-linked EOCs affecting the development of improved heat-shrinkable materials due to nanofillers acting as force concentrators in cross-linked structure [3]. The present study deals with investigation of electron beam irradiation response of ethylene-octene copolymer nanocomposites filled at a great ratio (0-15 wt%) of multi-walled carbon nanotubes (MWCNT) developed for heat shrinkable materials.

EXPERIMENTAL METHODS

Engage mark based EOC with octene content 17 wt% and BayerTM MWCNTs were used for development of composites. Obtained composites were irradiated with 5 MeV accelerated electrons up to 150-300 kGy. Tensile tests at 20-100 °C were conducted to determine their mechanical properties. The dynamic mechanical analysis was also performed. Thermomechanical behavior of the irradiated EOC/MWCNT samples, after their preliminary orientation by extension up to 100%, was investigated in the temperature range of 20-220 °C. The arising

thermal relaxation σ_{TR} and residual thermal shrinkage σ_{RS} stresses were determined by a strain gage equipped with a 0.01 N sensitivity. Gel fraction analysis and infrared spectra measurements were analyzed.

RESULTS AND DISCUSSION

The results of tensile properties at room temperature indicated slight increase of elastic modulus for EOC composites by 1.4-2.2 times with increase of filler content compared to EOC matrix, where by 1.2-fold elevated values were determined for cross-linked composites compared to non-irradiated ones.

CONCLUSION

Ethylene-octene copolymer nanocomposites with multi-walled carbon nanotubes up to 5 wt% were obtained with desired heat shrinkable properties thermal relaxation stresses >0.3 MPa and shrinkage stresses >0.6 MPa) and improved tensile properties. The results of FTIR analysis indicated that MWCNTs improved the resistance against oxidation of post irradiated composites thus enhancing their exploitation properties.

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PC/ABS nanocomposites with layered silicates: obtaining, structure and properties

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INTRODUCTION

Use of nanostructured functional fillers for modification of polymers has gained tremendous popularity in recent years partly due to the possibility of reinforcing a base polymer matrix at minor concentrations of nanofillers, typically not shared by their conventional microscopic counterparts.

Polymeric blends of polycarbonate (PC) and acrylonitrile-butadiene-styrene copolymer (ABS) are widely used in electrical and electronical equipment and form considerable part of electronic waste. It is not necessary that recycled and virgin polymer materials would show the same properties, but a good balance between properties and processability is absolutely necessary for recycled material [1, 2].

EXPERIMENTAL METHODS

The research has been devoted to evaluation of the effects of organically modified layered silicates (D43B, modified with dimethyl-, benzyl, alkyl amine) on the structural and mechanical characteristics of ABS (750 ABS SW, producer Kumho Petrochemical Co. Ltd), blends with PC (PC Calibre 303-15, producer Dow Chemical Company). Recycled PC was obtained from post-consumer CDs and DVDs, and recycled ABS was obtained from post-consumer computer parts. ABS content in the investigated composites was 10 wt%, while the content of nanoclay was varied in the interval between 0 and 2 wt%.

Polymer blends were obtained by using THERMO Electron co-rotating twin-screw extruder (temperature profile: 245-260 °C). Samples were obtained by injection molding (temperature profile: 250-280 °C; mold temperature 70 °C).

Thermal properties were measured by using DSC1/200W and TGA/DSC1 devices. Tensile strength/elongation properties were determined by using Zwick Roell BDO-

FB020TN universal testing machine. Impact strength was measured according to Charpy method.

RESULTS AND DISCUSSION

As expected virgin polymers (PC and ABS) and their blends show better mechanical, thermal and rheological properties in comparison to their recycled counterparts. Decrement of the properties of recycled multi-component polymeric systems, however, depends on the fraction of recycled material. Rise of the recycled polymer content up to 10 wt% does not considerably influence performance characteristics of the investigated systems. Mechanical and thermal properties of the investigated virgin and recycled composites are increased with addition of D43B.

CONCLUSION

Utilization possibilities of post-consumer PC and ABS from electronic waste are demonstrated. It is shown that properties of PC/ABS blends are not considerably affected unless the content of recycled polymer is not exceeding 10 wt%. Addition of D43B nanoclay leads to certain increment of mechanical and thermal properties of the PC/ABS based composites.

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Rheological properties of multi-component composites based on polymer-polymer matrix and nano-structured zinc oxide

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INTRODUCTION

Polypropylene is most valuable polymer if compare by production and consumption in Europe. Wide application possibilities in almost all markets make it very attractive: from packaging and agriculture, until special applications for laboratory equipment. Low UV and impact stability imposes limits on polypropylene use in wider range. Inferiorities of PP could be solved by addition of ethylene 1-octene copolymer and nano structured ZnO as it was observed in our previous works [1-4]. Quality of thermoplastic composites depends much on their melt behavior. Capillary rheometry gives possibility to evaluate melt flow process in a wide range of shear rates.

EXPERIMENTAL METHODS

Rheological properties were investigated for Polypropylene/Ethylene-1-octene copolymer/Zinc oxide (PP/EOC/ZnO) composites in a wide component range as showed in Table 1. Main polymer components were PP Basell Moplen HP456J and EOC Dow Engage 8200. Nano structured ZnO particles were synthesized in Institute of Inorganic Chemistry of Riga Technical University.

Material/ composite	EOC content wt. %	ZnO content wt. %
PP	0	0, 0.1, 0.5, 1, 2
PP90/EOC10	10	0, 0.1, 0.5, 1, 2
PP70/EOC30	30	0, 0.1, 0.5, 1, 2
PP50/EOC50	50	0, 0.1, 0.5, 1, 2

Composites were obtained by using two-roll mill Labtech Engineering Scientific LRM-S-110/T3E at roll temperatures of 175 and 165 °C and gap of 1 mm. Mixing occurred for 7 minutes. Obtained material was granulated and used for test. Rheological properties were characterized by using two-capillary rheometer Malvern Rosand RH-7. Bagley correction was applied by using orifice die (L/D=0.25/1 mm) in parallel to long die

(L/D=16/1 mm). Test temperature was 190 °C, shear rate range was from 5 till 5000 s⁻¹.

RESULTS

Shear rate, shear stress, viscosity, flow behavior index, extension rate, extension stress and extension viscosity of the composites were evaluated. For instance, in Fig.1 it is shown that flow behavior index *n* of the investigated systems decreases with addition of PP.

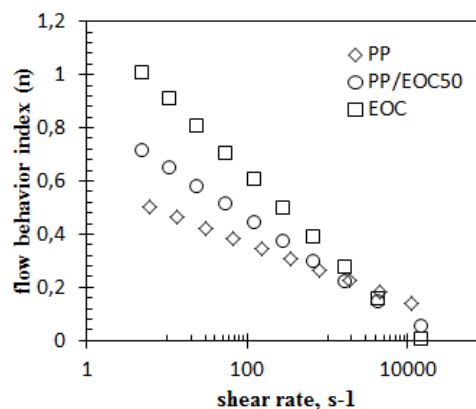


Fig.1. Flow behaviour index of PP, EOC and PP/EOC50 as function of shear rate

CONCLUSION

In the investigated shear rates range all the investigated PP/EOC compositions have character of pseudoplastic fluids, whereas pseudoplasticity of the melts is increased by rising the PP content, especially by considering that shear rate is below 1000 s⁻¹.

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Characterization of Polyvinyl Acetate/Multi Walled Carbon Nanotube Nanocomposites

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INTRODUCTION

In recent years solvent based approaches have gained attention as low cost and simple methods for obtaining of polymer-carbon nanotube nanocomposites. Recent studies of polyvinyl acetate (PVAc) nanocomposites demonstrate improvements in mechanical [1], thermal [2] and electrical properties [3].

EXPERIMENTAL METHODS

PVAc water dispersion (tradename Finndisp HW1) of 42 wt% solid content with average particle size approximately 3-4 μm was used as polymer matrix. Multi walled carbon nanotubes (MWCNTs) Baytubes C 150 P with outer diameter 13 nm and length 1-10 μm was used as filler. Sodium dodecyl sulfate was used to stabilize MWCNTs dispersion in water.

PVAc/MWCNT nanocomposites were obtained by dispersing MWCNTs in water, mixing with PVAc dispersion and casting in Teflon moulds. Then the material was allowed to dry in ambient temperature for 5 days.

Stress-strain characteristics of the obtained nanocomposite compositions were determined according to EN ISO 527 by using Zwick/Roell BDO-FM 020TN testing machine. Dynamic mechanical thermal analysis (DMTA) of the obtained nanocomposite compositions was carried out by using Mettler Toledo DMA/SDTA861.

RESULTS AND DISCUSSION

Stress-strain curves (Fig.1.) show increase in elastic modulus (E) and yield strength (σ_Y) by increasing the filler concentration up to 0.5 wt%. At the same time elongation at break (ϵ_B) significantly decreases. By increasing MWCNT concentration up to 2 wt% these properties do not exhibit further changes because of structural changes of the nanocomposites caused by MWCNTs

entanglements and even agglomeration as discussed elsewhere [4].

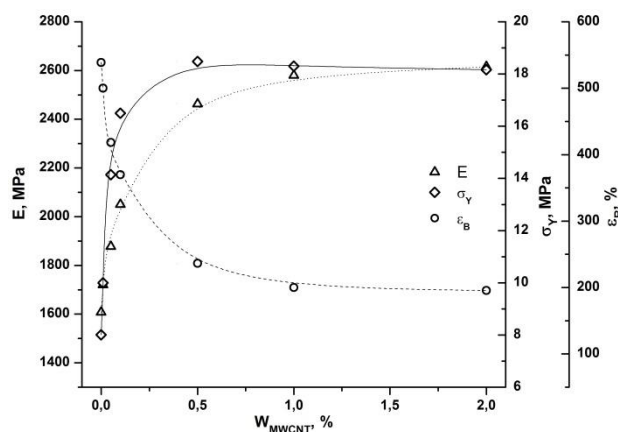


Fig.3 Main stress-strain characteristics of PVAc/MWCNT nanocomposites

DMA analysis revealed increase in E' modulus at low temperatures. It was also noticed that glass transition temperature of the nanocomposites was increased with addition of MWCNTs, testifying about the reduced molecular motion of the polymer macromolecules.

CONCLUSION

PVAc/MWCNT nanocomposites obtained by solvent casting presented increase in mechanical properties and raise in glass transition temperature in comparison to neat PVAc matrix.

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NiO and CoO promoted Pt catalysts for glycerol oxidation

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INTRODUCTION

A great attention has been paid to glycerol, as a biodiesel production by-product, in the recent years. Many possibilities of glycerol utilization have been studied, and catalytic oxidation is one of the preferable methods, where a number of important and valuable products can be obtained. Supported noble metal catalyst promotion with other metal additives is well-known. Usually promoters enhance catalyst's activity, but they also can change the direction of the reaction [1]. In this work, we reported the activity of the CoO and NiO promoted Pt catalysts supported on CeO₂.

EXPERIMENTAL METHODS

Pt supported catalysts were synthesized using extractive-pyrolytic method described in [2] and characterized by X-ray diffraction (XRD) and BET surface area analysis method.

Catalyst testing was performed in a thermostated slurry bubble reactor and in an autoclave reactor. The concentration of reaction products was analyzed by high-performance chromatograph Shimadzu Nexera. Oxidation of glycerol by molecular oxygen in presence of supported platinum catalysts was performed in alkaline water solutions.

RESULTS AND DISCUSSION

During the process of oxidation of glycerol in the presence of Pt/CeO₂ catalyst, the catalyst was active and selective to glyceric acid. As by-products lactic acid, glycolic acid, tartronic acid, oxalic acid and formic acid were obtained. CoO and NiO supported on CeO₂ composites, had poor activity in glycerol oxidation tests – glycerol conversion was less than 11%. As it is visible from Table 1, addition of CoO to supported Pt catalyst didn't enhance catalysts activity, but provided formation of glycolic acid as the main product with

selectivity of 40%, whereas NiO additive increased Pt/CeO₂ catalyst's activity – glycerol conversion increased by 19%. Elevation of partial oxygen pressure led to full glycerol conversion with a shorter reaction time and higher yield of glyceric acid (49%).

Catalyst	Glycero l conv., %	Selectivity		
		Glyceric acid	Lacti c acid	Glycoli c acid
Pt/CeO ₂	62	68	11	9
Pt/CoO/CeO ₂	62	17	11	40
Pt/NiO/CeO ₂	81	53	26	8
Pt/NiO/CeO ₂ [*]	100	49	13	7

Table 1. Oxidation of glycerol in the presence of monometallic 4.6wt%Pt/CeO₂ catalyst and in the presence of 4.8wt%CoO or 5wt%NiO promoted 4.6wt%Pt/CeO₂ catalysts. Reaction conditions: c₀(glycerol) = 0.3 mol/L; c₀(NaOH) = 1.5 mol/L, n(glycerol)/n(Pt) = 300 mol/mol; t = 60 °C, P(O₂) = 1 atm, oxidation time 5 h; (*-P(O₂) = 3 atm, oxidation time 4 h).

CONCLUSION

It was demonstrated that addition of NiO can promote supported Pt catalyst's activity. The best results (100% glycerol conversion and 49% selectivity to glyceric acid) were achieved in the presence of 4.6wt%Pt/5.0wt%NiO/CeO₂ over the following oxidation parameters: c₀(glycerol) = 0.3 mol/L, c₀(NaOH) = 1.5 mol/L, n(glycerol)/n(Pt) = 300 mol/mol, P(O₂) = 3 atm, t = 60 °C, oxidation time 4 h.

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Preparation of Nano-Sized Co₃O₄ by Pyrolysis of Organic Extracts

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INTRODUCTION

In recent years much attention has been paid to the production and application of Co₃O₄ catalysts in environmental catalysis. It is shown [1] that one of the factors which greatly affects the catalytic activity of Co₃O₄ catalysts is the method of production. The extractive-pyrolytic method (EPM) is a new promising method for the production of platinum supported catalysts [2]. This work presents the research results on the use of the EPM for the production of Co₃O₄ nanopowders and silica- and ceria-supported Co₃O₄ nanocomposites. The influence of the production conditions on the phase composition of the pyrolysis products and on the mean size of the cobalt oxide crystallites in the produced materials was studied.

EXPERIMENTAL METHODS

Cobalt-containing extracts (precursors) were produced by solvent extraction. Caproic acid (precursor 1) and a solution of n-trioctylamine in toluene (precursor 2) were used as extractants. Thermogravimetric measurements of the produced precursors were made using the LINSEIS STA PT1600. The pyrolysis products were characterized by X-ray diffraction (diffractometer D8 Advance, Bruker) and transmission electron microscopy (JEM-1230 operating at 100 kV). Magnetic measurements were made by a vibrating sample magnetometer (Lake Shore Cryotronics, Inc., model 7404).

RESULTS AND DISCUSSION

The main results of the performed experiments are summarized in Table 1. The presented data evidence that the use of precursor 1 makes it possible to produce a cobalt oxide powder with a smaller size of particles if compared with the use of precursor 2. The increase of the treatment

temperature (T_{pyr}) from 300 °C to 700 °C for the CeO₂ powder impregnated with the precursor 1 results in the growth of the mean size of the cobalt oxide crystallites in the composite (from amorphous to 20 nm). At the production of SiO₂/Co₃O₄ composites at $T_{\text{pyr}} = 700$ °C the cobalt oxides remains X-ray amorphous. If the SiO₂ nanopowder is impregnated with the precursor 2, then, with the treatment conditions being the same, a crystalline phase of cobalt oxides with $d_{\text{Co}_3\text{O}_4} = 35$ nm is formed on the carrier.

Sample	Pyrolysis T, °C	Anneal. time, min	$d_{\text{Co}_3\text{O}_4}$ from XRD, nm
Co ₃ O ₄ * powder	350	60	18
Co ₃ O ₄ ** powder	450	60	55
CeO ₂ /Co ₃ O ₄ * 5wt%	300	30	Amorp h.
	500	5	10
	700	5	20
SiO ₂ /Co ₃ O ₄ * 2.6wt%	500, 700	5	Amorp h.
SiO ₂ /Co ₃ O ₄ ** 2.6wt%	500	5	Amorp h.
	700	5	35

Table 1. Influence of the sample production conditions on the mean size of the Co₃O₄ crystallite with * - precursor 1, ** - precursor 2.

CONCLUSION

It has been shown that the mean size of the Co₃O₄ crystallites in the materials produced by the EPM varies from amorphous to 55 nm due to the production conditions.

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Synthesis of NiO nanoparticles by microwave assisted and molten salts methods

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INTRODUCTION

Nickel oxide nanoparticles due to its unique magnetic, optical, electronic and antibacterial properties are promising candidates for various applications. However, the mentioned properties depend strongly on the NiO particle size, and therefore on its preparation methods. At present various preparation methods of NiO nanoparticles have been developed. Recently NiO nanoparticles with size in the range of 20-25 nm, 50-80 nm were prepared by fast microwave assisted synthesis [1] and simple molten salts method at 1000 °C [2] respectively. However, synthesis temperature and NiO particle size were relatively high. At present work dependence of the size of NiO particle on microwave assisted and molten salts synthesis parameters were investigated.

EXPERIMENTAL METHODS

For molten salts method $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was mixed with NaCl - NaNO_3 at various molar ratio of the components. Mixture was heated at 350–700 °C for 2 h. The NaOH solution was added in separate experiments. Residual salts were removed by washing with distilled water and ethyl alcohol. For microwave assisted synthesis solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.002–0.004 M) and urea (0.005–0.100 M) in distilled water after stirring were transferred to PTFE-TFM container in microwave apparatus (Masterwave BTR, Anton Paar GmbH, 1700 W, 2.45 GHz). Synthesis was performed at 140–180 °C for 20 min. The obtained green precipitates were separated by filtration and calcinated up to 320 °C for one hour.

RESULTS AND DISCUSSION

According to XRD analysis the samples prepared by molten salts synthesis contained NiO without remarkable admixture of $\text{Ni}(\text{OH})_2$ because process temperature exceeds decomposition temperature of

hydroxide. The specific surface area and crystallite size of NiO particles were in the range of 15–24 m^2/g and 46–90 nm respectively depending on the temperature, molar ratio of nickel precursor and salts as well as on additive of NaOH . However, influence of the mentioned parameters on the particle size was weak and it did not allow reduce particle size in the large scale. Microwave assisted synthesis ensured formation of $\text{Ni}(\text{OH})_2$ or $\text{Ni}(\text{OH})_2$ with admixture of NiOOH depending on temperature, exposure time and concentration of chemicals. Additional calcination at 320 °C led to formation of NiO nanoparticles with specific surface area up to 106 m^2/g and crystallite size of 6 nm. Therefore, optimization of the parameters of the fast microwave assisted synthesis ensured essential lowering of the NiO particle size and procedure temperature.

CONCLUSION

Particle size of NiO prepared by molten salts synthesis is determined mainly by long exposure time.

Combining the fast microwave assisted synthesis at 140–180 °C with calcination at 320 °C is acceptable for preparation of NiO nanoparticles with crystallite size in the range of 5–8 nm.

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Improvement of the sorption characteristics of diatomite by heating treatment

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INTRODUCTION

The performance and efficiency of water treatment by adsorption technique predominantly depend on the nature of the adsorbent used. Therefore, several scientific researches are directed towards the development of new materials using different treatments to improve their adsorption capacities [1] [2]. For this purpose, we looked at the effect of heating treatment of naturally occurring diatomaceous earth (diatomite).

EXPERIMENTAL METHODS

The Diatomite used in this study is originated from Sig deposit (West of Algeria), to improve its characteristics for use in textile dyes adsorption the raw diatomite was treated at 100 and 300 °C in programmable furnace for 2h. The obtained materials were noted respectively Dt-100 and Dt-300. Firstly, some characterization methods were applied, to check what kind of modification has been occurred. After characterization, the obtained adsorbents were potentially studied for sorption of Orange Bezaktiv (SRL-150) textile dye.

RESULTS AND DISCUSSION

From the obtained results there is not drastic difference in the crystalline phases between the obtained materials Dt-100 and Dt-300. This treatment at 300 °C increases slightly in the specific surface area (from 11,09 to 16,12 m²/g) and in the volume of pores. The results of adsorption tests show, that the most suitable pH and equilibrium time were

respectively 2 and 30 min, at an adsorbent dosage of 2 g/L. The kinetic studies revealed that the adsorption results fitted very well with pseudo second order model ($R^2 = 0.9998$ and 0.9997 respectively for Dt-100 and Dt-300). Adsorption isotherms results were in accordance with Freundlich model more than the model of Langmuir.

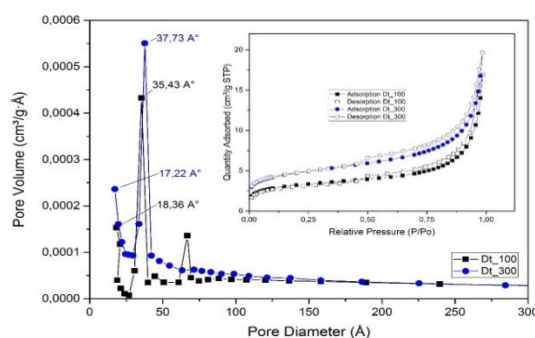


Fig.1. N₂ adsorption-desorption isotherms and corresponding BJH pore size distribution curve

CONCLUSION

The conclusions have to be based on the facts in evidence and should be limited to minimal speculation about the significance of the work.

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The authors would like to dedicate this work for the late Mr Prof. Ouali Mohand Said.

Use of mineral raw materials in water purification

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INTRODUCTION With the decrease of available natural resources, their price will significantly grow, thus making the recycling process more lucrative. Right now it is paramount to create purification systems which will give access to purified natural resources because in time the number of available natural deposits will become limited [1].

EXPERIMENTAL METHODS

Compositions were assembled by adding different ingredients. Resulting powder was milled again and homogenized in RETSCH RM100. Pellets were obtained by adding 10 mL of water for every 100g of powder. The solution was sifted through 0.5-2.5 mm sieves to give pellets with diameters 0.5-2.5mm respectively. Thermal work up was executed in NABERTHERM electrical furnace at 1090-1180 °C. Water sorption, porosity and density were tested as well as X-ray analysis (XRD). Iron saturation in solutions was measured after one day and seven days to determine whether its quantity increases over time.

RESULTS AND DISCUSSION

Density, porosity and water sorption was measured. Sample's B5 density is in range of 1.35 to 1.43, but increases to 1.65 at 1110 °C. Pellets with more quality are produced from material A5 at 1100 °C where porosity reaches 33% and 38-39% for sample B5 at the same temperature. Water sorption for sample B5 is 26-33% and 27-32% for sample A5. To determine whether all three pellets can be used as a sorbent for iron compounds in water solutions, an experiment was made. Further experiments were carried out by running a solution through a column which was filled with 50 mL pellets. Water samples were taken after specific interval - 30 and 60min.

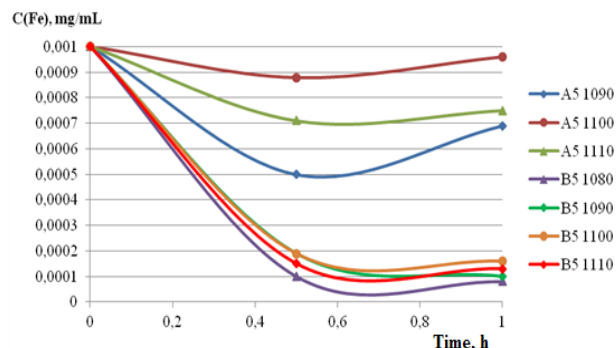


Fig.1. Changes of iron compound concentration depending on experiment time

Changes in iron concentration are shown in Fig.1.

CONCLUSION

Three samples were developed in this work. Sample following physical-chemical properties: density 1.35-1.65, water sorption 26-33% and porosity 38-44% shows the highest iron sorption qualities. A filter produced from named sample could potentially refine iron polluted water for 7 days and longer. Iron compound concentration shrinks by half.

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Different dip-coating technique impact on TiO₂ thin film properties

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INTRODUCTION In the past decades, an increasing interest has been devoted to the study of titanium dioxide thin films. TiO₂ finds a variety of applications such as desensitized solar cells [1], photoelectrodes, photocatalysts [2], gas sensors, and biomaterials due to its high activity, photochemical inertness, non-toxicity, good acid resistance, and low cost.

EXPERIMENTAL METHODS

To synthesize TiO₂ thin coatings the sol-gel method was used. The films were grown by two different dip-coating methods on a soda-lime silicate glass slide. In the first method (1×1×1), the substrate was immersed in sol at a speed of 220 mm/min, then dried at ambient temperature (20 °C) for 5 min. Then the coating was dried at 200 °C in a furnace for 5 min, and then calcined in the furnace at 500 °C for 1 h. In the second method (3×), substrate was immersed in sol at a speed of 220 mm/min and then dried at 200 °C in a furnace for 5 min. Then the coating was calcined in a furnace at 500 °C for 1 h. The film morphology, surface structure, and composition were investigated by X-Ray diffraction, atomic force microscopy optical properties were investigated by UV/VIS spectrophotometer and photocatalytic properties was investigated using a 125 W UV lamp.

RESULTS AND DISCUSSION

The particle size and average roughness of coatings are listed in Table 1. Particle size and roughness were measured from AFM images using the program Image Processing v. 2.1. From Figure 1 and Table 1, we can see clearly that the film structure obtained with the 1×1×1 method is a nanorod array with an average particle size of 95 nm and surface roughness of 5.34 nm. This coating structure provides good photocatalytic activity due to the small particle size and high contact angle.

Sample	Average roughness (nm)	Average particle size (nm)	Coating thickness (nm)
1x1x1	5.34	95	286
3x	22.88	495	412

Table 1 show the properties of TiO₂ sol-gel coating.

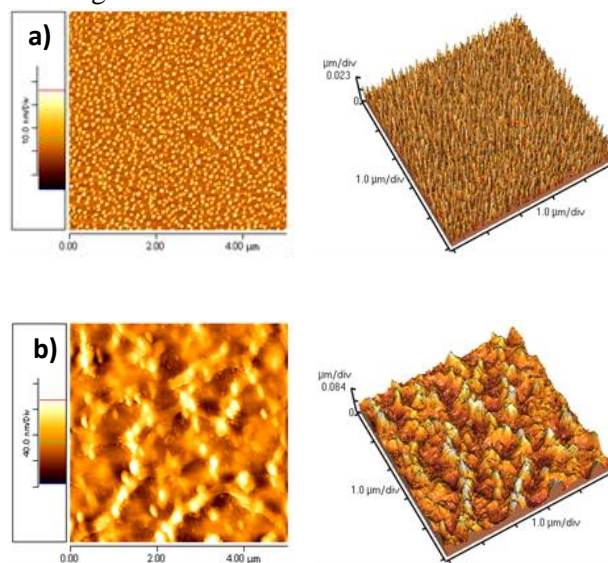


Fig.1. TiO₂ surface AFM images from a) 1x1x1 and b) 3x methods

CONCLUSION

From our results we can conclude that for multi-layer coatings the 1×1×1 method is better because with the 3× method, agglomerates are formed on the surface rather than single particles, reducing the quality of the coating. This coating with good light transmittance and photocatalytic activity and a great contact angle is promising for use in solar power receivers.

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Removal of Phosphates from Water Using Eggshell Bio Sorbents

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INTRODUCTION

Phosphorus is very important because of the significance of phosphorus as a vital factor in life processes. The phosphorus as biogenic element is an essential element for the growth of algae and cyanobacteria in the water. Such algal blooms do not occur when phosphorus are present in very limited amounts.

Eggshells are produced in large amount as domestic and industrial byproducts. Experience has shown that eggshells could be effective in waste water and different contaminated water treatment [1, 2].

This study explores the phosphate sorption by varying untreated and treated egg shell powders.

EXPERIMENTAL METHODS

Phosphate sorption experiments are studied at room temperature in static conditions and sorption kinetics are investigated. Phase composition, porosity, specific surface area, elemental composition and morphology of obtained bio sorbents are determined.

RESULTS AND DISCUSSION

Adsorption efficiency of the raw eggshells (Fig.1. top) and egg shell powder (Fig.1. bottom) are highly dependent on the mass of used adsorbent. Adsorption capacity of the raw eggshells reaches the maximum value of approximately 5 mg/g, which is compared with other low cost adsorbents adsorption capacities. The adsorption of phosphate ions onto raw eggshells is a result of specific chemical adsorption that occurs during formation of poorly soluble compound.

CONCLUSION

High phosphate adsorption efficiency of calcined eggshells determines the ability of this compound to be used as precipitation reagent for phosphorus removal from aqueous solutions.

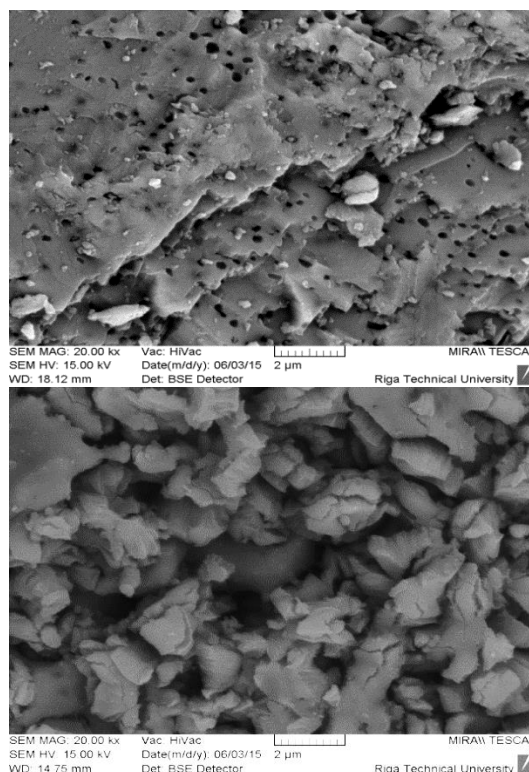


Fig.1. SEM micrographs of untreated (top) and calcined (bottom) egg shell powders

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Purification of Contaminated Water with Chromium (VI) using *Pseudomonas aeruginosa*

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INTRODUCTION

Hexavalent chromium is one of the most redoubtable metals, its toxicity is similar to that of heavy metals, and it may also be carcinogenic [1]. Several industries in sectors such as tanning, metallurgy, surface treatment, etc., produce important quantities of liquid waste containing chromium Cr(VI) [2]. The minimum allowable concentration for Cr (VI) required is around 0.1 mg/L. To be in this acceptable limit of concentration, it is important for these industries to treat their effluent before releasing. The removal of hexavalent chromium is a major environmental problem, since the costs of existing conventional treatments are very high [3]. For this purpose, a bacterial strain *Pseudomonas aeruginosa* isolated from an uncontaminated soil has been used for the removal of hexavalent chromium (Cr (VI)).

EXPERIMENTAL METHODS

The experiments were carried out in batch system in a culture broth. *Pseudomonas aeruginosa* was isolated from an agricultural soil. Samples were collected from Mostaganem area (west of Algeria). The physiological and biochemical tests were carried out for its identification. *Pseudomonas aeruginosa* was incubated at 37 °C in a liquid medium (pH of 7.2). For the determination of the residual concentration of chromium (VI), we followed the protocol using the diphenylcarazide complexation.

RESULTS AND DISCUSSION

The results obtained have shown that 100% of Cr(VI) are removed. Contact time, initial concentration of the hexavalent chromium, temperature, as well as the nature of the culture broth have influenced this

elimination. To the initial concentration of 20 g/L of Cr (VI) the elimination rates are lower due to toxicity of the metal.



Fig.1. *Pseudomonas aeruginosa* culture

CONCLUSION

This study allows considering the use of *Pseudomonas aeruginosa* in the treatment of water polluted by toxic heavy metals such as Cr (VI).

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The authors would like dedicate this work to Prof Mohand Said Ouali.

Adsorption of Lead (II) In Liquid-Solid Interfaces on Natural and Modified Hydroxiapatite

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INTRODUCTION

Many industries, such as the petrochemical, painting and coating, newsprint, smelting, metal electroplating, mining, plumbing and battery industries, discharge lead (Pb) into the environment without adequate purification in some cases. Lead may be transported into water bodies by natural circulation and therefore threaten human life due to its well-known toxicity, accumulation in food chains and persistence in nature. Unlike organic compounds, lead is non-biodegradable, and, therefore, must be removed from wastewater [1, 2].

Therefore, in this study, we are interested to use the natural phosphate mineral which is considered cheap [3]. We try to highlight the importance of effective use of such materials for the purification of water containing heavy metals especially lead element.

EXPERIMENTAL METHODS

The hydroxyapatite samples come from Djebel Onk (East Algeria). After grinding and sieving (250 μm), 20 g of natural hydroxyapatite (HAPr) was mixed for 24 h with 100 ml of 5% lactic acid solution. The suspension was centrifuged and the supernatant was washed several times with distilled water. Then, the resulting material (HAPal) was dried at 80 °C for 48 h.

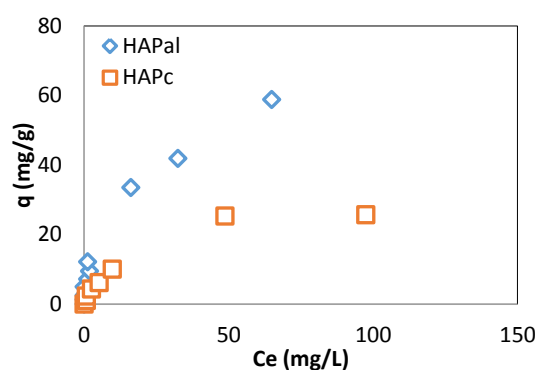


Fig.1. Extraction isotherm of lead (II) at ambient temperature (25 °C)

CONCLUSION

Finally, the results of this study allow us to note that the hydroxiapatite material can be as good extractant solid, for heavy metals, especially when it is modified with lactic acid.

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The level of inflammatory cytokines and antimicrobial peptides after composite material implantation and contamination with bacterial culture

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INTRODUCTION

Due to the fact that biomaterial implantation is a traumatic process, especially if the implanted object is contaminated by bacteria, it can cause a significant inflammatory cytokine production, or the opposite – its suppression. The aim of this study is to evaluate the expression of inflammatory cytokines (IL-10, beta-defensin-2 and TNF-alpha) in surrounding tissues of implanted biomaterials *in vivo* [1].

EXPERIMENTAL METHODS

Biomaterial samples (hydroxyapatite with gentamicin, hydroxyapatite with gentamicin and biodegradable polylactic acid polymer, hydroxyapatite with biodegradable polylactic acid polymer) were implanted in subcutaneous pockets of chinchilla rabbits and the implantation wound was contaminated with *Ps. aeruginosa* (ATCC 27853) or *S.epidermidis* (ATCC 12228) bacterial culture. Four weeks later, using standard ELISA kits (USCN life science and MyBioSource, USA) according to the manufacturer's instructions, the level of IL-10, TNF-alpha and beta-defensin-2 was determined in directly surrounding tissues around the biomaterial and in tissues within a distance of 1.5 cm from the biomaterial. Healthy chinchilla rabbits were used as a control group. The Mann-Whitney test was used to assess whether there is a statistically significant difference between antibacterial times of different biomaterial samples. It was assumed as statistically significant if *p* value was less than or equal to 0.05. Statistical analysis was performed with SPSS 22.0.

RESULTS AND DISCUSSION

In comparison to the control group, normal levels of inflammatory cytokines were

found in the direct tissue area around biomaterial samples and in the distance tissue area after implantation of biomaterials with gentamicin and wound contamination with *Ps.aeruginosa* and *S.epidermidis*. In comparison to the control group, statistically significantly higher levels of inflammatory cytokines were found in direct tissue area around biomaterial samples and distance tissue area after implantation of biomaterials without gentamicin and wound contamination with *Ps.aeruginosa* and *S.epidermidis*.

CONCLUSION

An increased level of inflammatory cytokines (IL-10, beta-defensin-2, TNF-alpha) indicates an active inflammatory process after biomaterial implantation without gentamicin and contamination with bacterial cultures. The practical use of biomaterials impregnated with antibiotics may reduce the expression of inflammatory cytokines in tissues surrounding implanted devices.

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Impact of Biphasic Calcium Phosphate (BCP) Bioceramics on Osteoporotic Hip Bone Mineralization *in vivo* Six Months After Implantation

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INTRODUCTION

BCP as bone substitute is successfully used for local recovery of osteoporotic bone and filling of bone defects [1]. Experimental and clinical data confirmed bioactivity of synthetic hydroxyapatite in bone environment through activation of endogenous growth factors and mineralisation of atrophic host bone [2]. In current study we evaluated response of osteoporotic bone to implantation of BCP granules with HAp/ β -TCP ratio of 90/10.

EXPERIMENTAL METHODS

CDHAp was synthesized by aqueous precipitation technique from calcium hydroxide and phosphoric acid and sintered granules in size range from 0,5 to 1 mm were prepared as described before [3]. Minor micro porosity with pore sizes around 200 nm was observed for obtained materials. With permission of Latvia Republic Food and Veterinary Administration, nine female rabbits with induced osteoporosis by ovariectomy with following injections of methylprednisolone 1mg/kg daily for 8 weeks were examined in current experiment. On six of animals, 3 mm hole was created in hip bone and filled with prepared BCP granules. Control group of three rabbits with similar bone defect were left without BCP implantation. After 6 months animals were euthanized, bone samples collected and proceeded for detection of osteocalcin (OC), osteopontin (OP) and osteoprotegerin (OPG) immunohistochemically. Appearance of these factors was evaluated semiquantitatively [4].

RESULTS AND DISCUSSION

Controls showed decreased number of long, thin bone trabeculi intermixed by bone

marrow. Also the number of osteocytes was notably decreased. All together these changes proved the presence of experimental bone osteoporosis. In experimental group bone showed partially resorbed bioceramic granules surrounded by osteoclasts and connective tissue capsule of different thickness. In some samples new bone formation near the granuli was observed.

In all samples of the experimental group, number of OC positive cells increased more than twice as to compare to the control. Also increased expression of OPG (moderate to numerous positive cells) in visual field was observed. However, increase in number of OP-containing osteocytes was less obvious.

CONCLUSION

Implantation of BCP HAp/ β TCP 90/10 bioceramic granules in osteoporotic rabbit bone increases expression of OC and OPG indicating the activation of osteoblastogenesis and bone mineralization *in vivo* along the more “rigid” stabilization of bone homeostasis (slow OP increase).

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ACKNOWLEDGMENTS

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Response of Osteoporotic Jaw Bone to Implantation of Biphasic Calcium Phosphate (Hap/ β -TCP) Bioceramics supplemented with Autologous Mesenchymal Cells (MSC)

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INTRODUCTION

Synthetic β -TCP implanted into critical sized bone defect of rats with experimental osteoporosis demonstrated better effect to bone tissue repair in osteoporosis and/or osteoporosis status [1]. Stem cell transplantation may improve bone mineral density in animal models of osteoporosis [2]. Combination of BCP and stem cells are not studied on old experimental animals with double induced osteoporosis as with permission of Latvian Republic Food and Veterinary Administration was done.

EXPERIMENTAL METHODS

Experimental osteoporosis was induced in 10 2,5 years female rabbits by ovariectomy under general anesthesia followed by 1 mg/kg of methylprednisolone daily for 8 weeks. During the first surgery fat tissue were collected, selection and cultivation of mesenchymal cells done. Under local anesthesia on 4 animals the holes on the left side of lower jaw were filled with a HAP/ β -TCP 90/10 granules; on the right side the same granules mixed with autologous fat tissue-derived mesenchymal cells implanted. Samples were taken out after three months, histological specimens stained with Hem/eos and Masson trichrome and evaluated with light microscopy. The two control groups each consisted of 2 rabbits – with the analogous defect of osteoporotic jaw bone without bioceramics and without any defect.

RESULTS AND DISCUSSION

We chose old experimental animals and HAP/ β -TCP 90/10 bioceramics because in cases of weak bone potencies to regeneration as in severe osteoporosis when resorption of β -TCP may go ahead of new bone formation and obtained volume of augmentation may be lost.

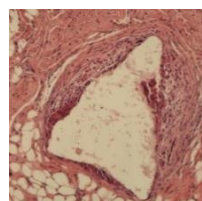


Fig.1. Tissue response around granule three months after implantation of HAP/ β -TCP 90/10 without cells. Granule surrounded with connective tissue. Macrophage reaction in contact with granule. Hem/eos, X 200

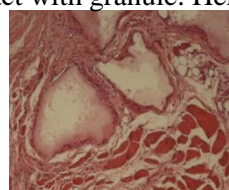


Fig.2. Controle without experimental osteoporosis. Chain of osteoblast like cells around granules. Hem/eos, X 200

Not only bone but also fat tissue as source of stem cells in old animals have decreased regenerative potency.

CONCLUSION

In osteoporotic bone 3 months after implantation fibrous connective tissue capsule without evident inflammation reaction was observed around the bioceramic granules.

Histological sign of osteoblastic differentiation as chain of osteoblast – like cells around granules was in the same age animals without experimental osteoporosis.

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Synthesis and Properties of α -Tricalcium Phosphate from Amorphous Calcium Phosphate as Component for Bone Cements

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INTRODUCTION

Calcium phosphate bone cements are widely known materials for augmentation, substitution and regeneration of bone tissue. Most cements that set to form hydroxyapatite (material similar to inorganic phase of bone tissue) require starting materials that are synthesized at temperatures exceeding 1200 °C and require milling after synthesis. Relatively recently new methods for preparation of these materials that require lower synthesis temperatures and no milling step have emerged [1-4]. These materials offer a possibility to modify the properties of already existing cement types.

The aim of this study was to examine the synthesis of α -tricalcium phosphate (α -TCP) from amorphous calcium phosphate (ACP) precipitated from aqueous solutions. In particular this study examines the influence of thermal treatment on the obtained particles.

EXPERIMENTAL METHODS

ACP was precipitated in batches by adding 160 mL 0.3 M calcium nitrate solution and 70 mL 0.45 M diammonium hydrogen phosphate to 90 mL of concentrated ammonia solution at room temperature. The resulting suspension was immediately centrifuged and rinsed with deionized water. The resulting precipitate was then freeze-dried and then further dried at 120 °C. The dried precipitate then was heat treated at various temperatures from 500 °C to 900 °C to produce α -TCP. The reactivity of produced α -TCP was assessed by speed of hydrolysis in presence of water at 37 °C. The phase composition of heat treated precipitate and hydrolysed products was determined using XRD.

RESULTS AND DISCUSSION

The heat treatment of obtained XRD-amorphous precipitate produced almost pure α -TCP. SEM images showed partially sintered (connected) particles with 100–250 nm depending on the heat treatment temperature.

The hydrolysis characteristics of obtained α -TCP sub-micron sized particles were compared to those of prepared at high-temperature (1300 °C) and milled. The hydrolysis speed α -TCP sub-micron sized particles was slower than of high-temperature α -TCP milled for 4 h, but faster than that of high-temperature α -TCP milled for 1 h.

For the first time the heat treatment of ACP to obtain α -TCP has been systematically examined and the reactivity of obtained particles evaluated.

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Bovine serum albumin adsorption onto hydroxyapatite and biphasic calcium phosphate ceramic granules

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INTRODUCTION

Hydroxyapatite (HAp), beta tricalcium phosphate (β -TCP) and biphasic calcium phosphate (BCP) are calcium phosphate based ceramics and the most studied biomaterials for bone defect repair [1]. One of the main requirements for these biomaterials is to be bioactive. The bioactivity of calcium phosphate based biomaterials can be evaluated by adsorption of proteins [2]. The most abundant protein in the circulatory system is bovine serum albumin (BSA) therefore this protein is mostly used in vitro studies for bioactivity [3]. BSA sorption results onto HAp and BCP ceramic granules are presented.

EXPERIMENTAL METHODS

HAp and BCP were synthesized by wet precipitation method from calcium hydroxide and phosphoric acid. To identify the ratio of HAp and β -TCP phases X-ray powder diffraction (XRD) was used. The precipitate were filtered and used to form granules. The paste was pressed through 1.4 mm sieve, dried, sieved through 1.4 mm sieve, sintered at 1150 °C for 2 h and sieved using vibrational sieves to gain granules with fraction 0.5-1 mm. The obtained fraction was characterized with loose density and specific surface area by BET method. Protein solutions were prepared in simulated body fluid (SBF) and phosphate saline buffer (PBS) solution at pH 7.4 by dissolution of BSA with concentration 2 mg/ml. 0.1 g of granules were mixed with 8 ml of BSA solution and incubated at 37 °C with continual agitation for 5 minutes to 24 hours. The residue concentration was determined at 280 nm using UV-VIS spectrophotometer. All calibration solutions also were incubated at 37 °C and measured each time together with the samples.

RESULTS AND DISCUSSION

The highest sorption capacity (mg BSA/1 g granules) showed sample with HAp/ β -TCP ratio 50/50 but the lowest sorption showed sample 10/90 in both SBF and PBS media. These results are related to the specific surface area (see Table 1). In SBF media the adsorbed BSA amount is more than 2 times higher than in PBS.

Table 1 Characteristics of the samples studied

COMPOSITION HAp/ β -TCP	LOOSE DENSITY, g/ml	BET, m ² /g
100/0	1.19 ± 0.01	0.92 ± 0.10
80/20	1.06 ± 0.01	0.80 ± 0.07
50/50	0.99 ± 0.01	1.13 ± 0.03
30/70	1.10 ± 0.01	0.80 ± 0.04
10/90	1.23 ± 0.02	0.05 ± 0.01

CONCLUSION

All calcium phosphate ceramic granules showed sorption properties towards BSA in both media. BSA sorption capacity correlates with the specific surface area.

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Preparation and characterization of strontium ranelate loaded microcapsules

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INTRODUCTION

Musculoskeletal disorders such as osteoporosis are becoming a great problem all over the world. Strontium ranelate (SrRan), a novel orally active agent consisting of two atoms of stable strontium and the organic moiety ranelic acid, has proven drug ability to increase not only the bone mass but also mechanical properties [1]. Despite the advantages it has been shown that systemic administration of SrRan can cause such side effects as diarrhea, hypersensitivity and myocardial infarction [2]. Microencapsulation of SrRan could be a novel way to avoid the possible side effects from the systemic drug use as well as to increase its efficiency by local delivery of drug right to the affected bone site. Thus in the current research an attempt was made to prepare and characterize poly(lactic acid)/strontium ranelate microcapsules.

EXPERIMENTAL METHODS

SrRan loaded poly (lactic acid) microcapsules were prepared using slightly modified microencapsulation method described elsewhere [3]. Briefly, SrRan was properly homogenized with 7% PLA solution in methylene chloride, added to the 4% aqueous PVA solution and emulsified for 60 s at 7000 rpm. After emulsification organic solvent was extracted in water, microcapsules formed were separated by centrifugation for 1 min at 1000 rpm and dried at 40 °C for 24 h.

Scanning electron microscopy (SEM) was used to evaluate the microparticle surface morphology and inner structure. Microanalysis was used to determine the nitrogen content in samples. Average microcapsule size and particle size distribution were determined using a laser particle size analyzer. SrRan release from

microcapsule (MK) samples was determined via UV/VIS spectroscopy at 325 nm.

RESULTS AND DISCUSSION

During the microencapsulation process such parameters as SrRan solid load in the organic phase (Fig.1 C) and water amount in primary water phase (Fig.1 B) were changed. Parameter changes resulted in SrRan containing microcapsules with total drug load in the range from $3,02 \pm 0,36$ wt% up to $6,60 \pm 1,29$ and drug encapsulation efficiency from $4,64 \pm 0,02\%$ up to $23,85 \pm 5,25\%$.

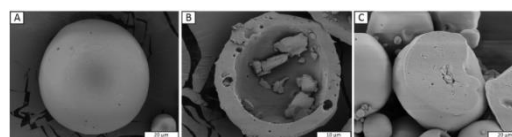


Fig.1. SEM microphotographs of: A) PLA/SrRan microcapsule surface; B) PLA/SrRan microcapsule cross section (using s/w/o/w method); C) PLA/SrRan microcapsule cross section (using s/o/w method)

CONCLUSION

During the study it was found that in order to increase the SrRan load in the prepared microcapsules and the drug encapsulation efficiency, the drug crystal size should be decreased at least for 2 times and s/w/o/w method should be used.

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Characterization of Crystalline Structure and Morphology of Ga₂O₃ Thin Film Grown by MOCVD Technique

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INTRODUCTION

Gallium oxide (Ga₂O₃) is a wide band gap (~5 eV) material possessing good optical and electrical properties and therefore hosting a range of potential applications, from high voltage transistors [1] to optoelectronic devices.

EXPERIMENTAL METHODS

This work is devoted to characterization of crystalline and morphological properties of gallium oxide (Ga₂O₃) thin films. Samples were produced by metal organic chemical vapor deposition (MOCVD) on sapphire substrates using trimethylgallium and water as precursors. Structural and compositional properties were evaluated using XRD and PL. Surface morphology was taken by AFM and SEM.

RESULTS AND DISCUSSIONS

Conducted XRD measurements indicate that grown Ga₂O₃ film possess monocline polycrystalline structure. PL measurements shows wide band luminescence from 2 to 4 eV with corresponding excitation band from 5 to 8 eV. SEM and AFM investigation shows specific surface structure features with overall roughness within 10 nm.

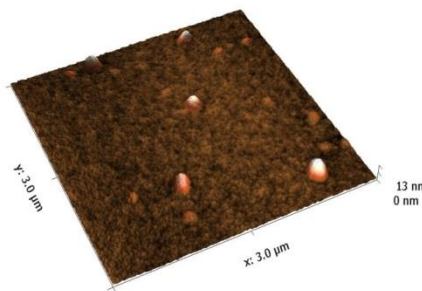


Fig. 1 AFM image of β - Ga₂O₃ thin film

CONCLUSION

Obtained thin films were characterized as polycrystalline β - Ga₂O₃.

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Synthesis of the Gadolinium-Yttrium-Aluminum Garnet by Spraying of Aqueous Salt Solutions

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INTRODUCTION

Compounds with the structure of garnet with the general formula $R_3Me_5O_{12}$ are used in industrial and medical tomography, solid-state lasers materials, radiometry [1]. Classical methods of production of the materials with garnet structure is to grow single crystals from the melt, solution and gas medium. These methods are laborious and often can not provide the required homogeneity. Other way to obtain these materials is a production of optical ceramics out of high purity powders as a starting materials. In this study spray drying method is explored for synthesis of complex oxides powders with garnet structure. The spray drying method allows to obtain fine powder of high purity with a capacity up to 500 g/h, it is a promising method for the synthesis of such materials.

EXPERIMENTAL METHODS

Powders were synthesized by spray-drying method on Buchi Spray Dryer B-290. A water solution was prepared from the nitrates of aluminum, yttrium, gadolinium and cerium basing on the stoichiometric ratio of these elements in a given composition of the synthesized composite oxide: $Y_xGd_{(3-x)}Al_5O_{12}:Ce$ Al:Gd:Y:Ce=5:(3-X):X:0.004. The prepared solution was fed through the spray nozzle installed in the drying chamber where it was mixed with a stream of hot air. After synthesis, the obtained powder was subjected to heat treatment in air at temperatures ranging 300-1150 °C.

The synthesized powders were investigated by thermogravimetric and differential thermal analysis. The powders size and morphology were observed by scanning electron microscopy. Phase composition was investigated by X-ray diffraction analysis.

RESULTS AND DISCUSSION

During the drying in the air flow the full or fractional decomposition of the salt occurred and a dry oxide-salt product forms. Fig.1,a shows micrographs of the as-synthesized powder.

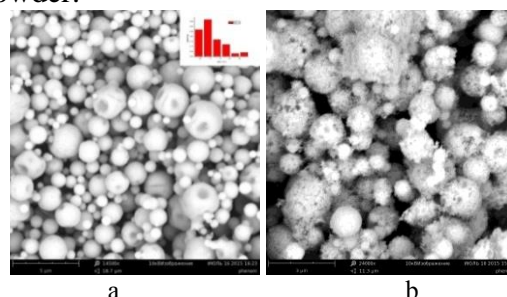


Fig.1. Photomicrographs of the as-synthesized (a) and heat treated at $T_a = 500\text{ }^{\circ}\text{C}$ for 1 hour, and $T_a = 1150\text{ }^{\circ}\text{C}$ for 3 hours (b) powders

The synthesized powders were subjected to heat treatment at 500°C for total salts decomposition and formation of the oxide material. As revealed by XRD the annealed at 500°C oxide powders are still amorphous. Crystallization begins at temperatures of 800- 900°C and goes in several stages. The final product of the crystallization is oxide with garnet structure. The photomicrographs of the garnet powder is shown in Fig.1,b.

CONCLUSION

The study shows the possibility of production of sub-micron powders of complex oxide with garnet structure by spray drying method. The possibility of the synthesis of a single-phase structure of garnet over the entire range of compositions $Y_xGd_{(3-x)}Al_5O_{12}$ was demonstrated.

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Complex XPS and Raman Study of Graphene Undergone to Different Treatments

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INTRODUCTION

Nowadays graphene has become one of the most popular materials for nano- and optoelectronic applications. X-ray photoelectron and Raman spectroscopies are the basic analytical methods used for the characterization of carbon based materials especially graphene related ones [for example, 1, 2]. However, matching XPS and Raman data is often non-obvious and controversial. The present work is devoted to a complex – XPS and Raman - study of graphene materials synthesized by chemical vapor deposition (CVD) and undergone to different treatments.

EXPERIMENTAL METHODS

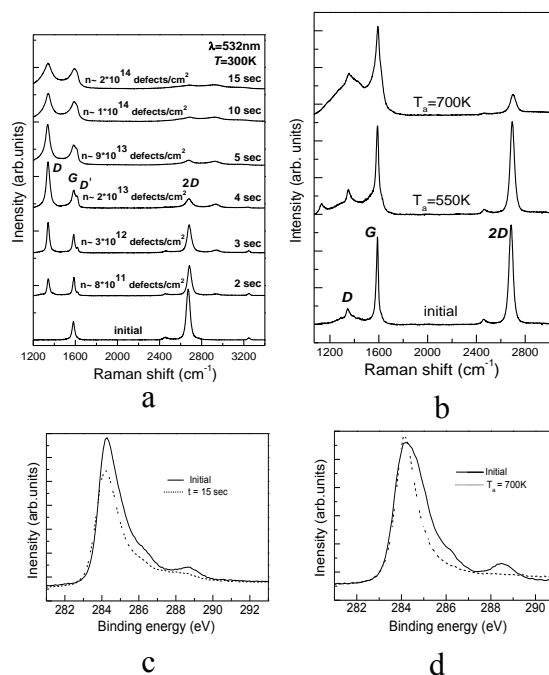
Graphene samples were synthesized by CVD processes on copper substrate and transferred on Si/SiO₂ by standard technology. Synthesized samples were exposed to various treatment - Ar⁺ bombarding, mild oxidation and heat treatment in reduction atmosphere. Raman spectra were measured by micro-Raman at room temperature on Horiba Jobin-Yvon T64000 and LabRam HR800, equipped with confocal microscope, which allowed to obtain information from the area of about 1 mkm. XPS analysis was performed on Thermoscientific K-alpha using an Al K-alpha X-ray source. C1s, O1s, Cu2p and Si2p peak data were collected to analyze thickness and a fraction of functional groups.

RESULTS AND DISCUSSION

It was found by XPS that Ar⁺ bombardment of graphene results in the etching of the functional groups and carbon itself with subsequent deposition from the atmosphere at exposing to air (Fig.1,c). Those phenomena were reflected in a degradation of graphene structure

revealed by Raman spectroscopy (Fig.1,a). The heat treatment in H₂ atmosphere results in the reduction of the functional groups (Fig.1,d). However, this process as well leads to an introduction of defects to the graphene structure (Fig.1,b). The origin of the defects introduced by different treatments are discussed basing on the XPS and Raman results.

Fig.1. Raman (a, b) and XPS (c, d) spectra of graphene after Ar⁺ bombardment at 500eV (a, c)



and heat treatment in H₂/Ar atmosphere (b, d)

CONCLUSION

A complex (XPS and Raman) study of graphene materials synthesized by CVD has been made. The defects introduced by the different treatments are discussed.

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Study of Surfaced Cutters for Machining of Wood-Based Materials

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INTRODUCTION

Wood is probably the best known natural composite material in which cellulose fibres are arranged in bunches and are bonded with lignin. The dramatic decrease of natural wood resources in the World related with the need to use wastes from natural wood manufacturing, have made further improvements of wood-based composite materials highly essential. Combining wood with other materials allowed to develop composites with specific properties, which are often better than the properties of natural wood. To achieve the highest properties, special techniques and machining tools are required. Evolution of wood cutting tool materials, as well as new implementation of new techniques, helped to process wood-based composite materials efficiently ensuring a high quality product. Although new tools and techniques have been developed and are in use, there is a need for a better understanding of the properties of wood-based materials and of the factors influencing the machining process. Medium density fibreboard (MDF) is an engineering wood-based material used for variety of furnishing, industrial, and for interior/exterior construction applications, because of its applicable properties such as surface appearance, dimensional stability and excellent machinability.

EXPERIMENTAL METHODS

The present study describes results of recent research aimed to make high wear resistance cutter for machining of wood-based materials. Medium density fibreboard (MDF) was chosen for wear test because it is quite abrasive, ease blunts edges of cutters, is inhomogeneous material: contains glue and different mineral particles. It is well known that cutting particleboard results in wearing out of cutter faster than machining of natural wood [1]. Because of this, experimental cutters made by surfacing using submerged arc welding (SAW)

technique and prepared material powder mixture spread on the surface of cutters blank, were introduced in this research. Wear resistant coatings were surfaced on skived surface of cutter blank made of cheap plain carbon steel. The surfacing process was performed in a single pass using alloying materials mixture (~ 6 g) spread on the surface under the flux. Before surfacing each sample was mechanically polished. Suggested material powder mixture ensured obtaining the high alloyed and wear resistant surface layer on the cutting edge of cutter. The wear performance of experimental and commercial cutter was accomplished on the typical industrial thickness planer with a face milling cutterhead using MDF as workpiece.

RESULTS AND CONCLUSIONS

The results showed that application of surfacing using submerged arc welding technique and materials powder mixture spread on the surface of substrate under the flux, increased wear resistance of experimental cutters for machining of wood-based materials. Shank of experimental cutter was made of plain carbon steel with alloyed high wear resistant working edge. So, using suggested technology it is possible to reduce expenses of machining of wood-based products, and to recycle industrial waste (metal machining waste was used for the preparation of powder mixture). Summarizing the achievements of presented study, the following can be stated: relatively hard coatings (50-63 HRC) surfaced on a cutter blank made of soft plain carbon steel can replace some commercial cutters made of high speed tool steels for machining of wood-based materials.

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Stability of suspensions and emulsions containing illitic clays

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INTRODUCTION

Clay minerals are widely used in cosmetic products as of suspensions and emulsions. These both forms are thermodynamically unstable and the phases separate in time. Suspensions are stabilized with stabilizing agents (electrolytes) [1], but emulsions - with surfactants (usually molecules with both polar and non-polar groups) and solid particles. Application of solid particles instead of surfactants is attractive to production of cosmetic and pharmaceuticals due to possible harmful effect on human [2]. The addition of clay minerals to suspensions and emulsions improve their stability. From clay minerals montmorillonite, kaolinite, laponite and paligorskite are mostly investigated and used [1, 3], but research show that illite containing clay minerals also can stabilize oil-in-water emulsion [4]. Stability of emulsions containing natural clays at high solid content is mostly controlled by the tri-dimensional network formed by clay particles [3]. Stability of suspensions and oil-in-water emulsions containing illitic clays was investigated.

EXPERIMENTAL METHODS

Clay samples from Latvia - Iecava (Ie), Laža (La) and Pavāri (Pa) with fraction under 2 μm were used. A part of the samples was treated with 1M HCl for removal of carbonates and also with sodium dithionite to remove iron containing compounds. Suspensions were prepared from 50 and 90% glycerol with clay concentration 20 and 5 mass%, respectively. Emulsions were prepared from safflower oil with oil-water ratio 1:2. Zeta potential of all suspensions was measured. Viscosity and stability of all suspensions and emulsions was investigated. For emulsions the stability was quantified by the time period during which no significant creaming could be visually observed.

RESULTS AND DISCUSSION

The viscosity and stability of clay sample suspensions and emulsions increases in order: treated with dithionite < treated with HCl < untreated (see Fig.1). Clay samples treated with dithionite showed the highest zeta potential.

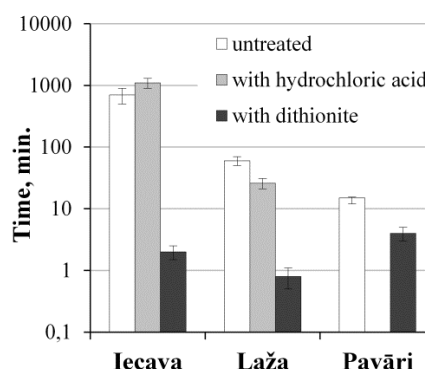


Fig.1. Stability of emulsions containing illitic clay with concentration 5 mass%

CONCLUSION

The stability of suspensions and emulsions decreases when the net negative charge on clay mineral particles increases, but the stability increases when viscosity of clay fraction suspension increases.

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Synthesis of Eu^{2+} and Dy^{3+} doped nanosized strontium aluminates and their properties

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INTRODUCTION

Last years the luminescent properties of $\text{SrO-Al}_2\text{O}_3\text{-Eu-Dy}$ system have attracted much attention [1]. Strontium aluminates doped with rare earth ions were observed to be efficient light emitter and found many applications as long afterglow phosphors [2]. They are used in safety and emergency signs, in plasma screens, fluorescent lamps and light diodes. In this study we developed solution-combustion synthesis method of strontium aluminates and investigated their properties depending on parameters of synthesis.

EXPERIMENTAL METHODS

Strontium aluminates were prepared from metal nitrate solutions and organic fuel. Different concentrations of dopants (Eu, Dy) and three combustion agents (urea, glycine, citric acid) were used. Additional flux of boric acid was added for better crystallinity. Precursor solution was heated to dehydrate. The combustion reaction was completed in few minutes resulted in fluffy voluminous powder.

RESULTS AND DISCUSSION

Obtained powders were calcinated at temperature 900, 1000 and 1300 °C (Fig.1.). XRD measurements showed the main phase of SrAl_2O_4 and traces of $\text{Sr}_3\text{Al}_2\text{O}_6$, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$. The intensity of luminescence was highest for samples containing smaller concentration of dopants (1 mol% Eu and 1 mol% Dy). The specific surface area varied from 5.7 to 38.9 m^2/g , and crystallite size varied from 30 to 80 nm depending on temperature of calcination, used fuel, and content of dopants (Table1).

Photoluminescence spectrum of $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} showed emission maxima at 525 nm and it did not depend on used organic fuel.

SAMPLE No	CALCINATION TEMPERATURE, °C	CRYSTALLITE SIZE, nm
1	900	20 – 30
2	1000	50 – 60
3	1300	80

Table 1. Dependence of crystallite size on the calcination temperature.

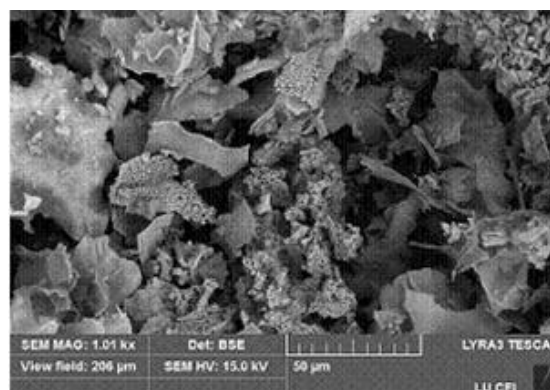


Fig.1. $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Dy}^{3+}$ SEM image

CONCLUSION

Combining combustion synthesis of strontium aluminate with calcination at 1300 °C ensured preparation of $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Dy}^{3+}$ particles with crystallite size of 80 nm with minimal content of extraphases. Intensity of photoluminescence depended on the content of dopants.

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Preparation of B₆O materials via reactive and non-reactive spark plasma sintering

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INTRODUCTION

Boron suboxide B₆O is promising chemically inert wear resistant material with hardness close to that of well-known superhard materials – cubic boron nitride, diamond. However parameters of B₆O materials depend strongly on their preparation methods, density and microstructure. Commonly B₆O materials are fabricated via fast non-reactive or reactive sintering methods using sintering additives such as metals or oxides of transition metals [1], leading to high density and formation extra phases of additives borides. The aim of present work was to compare sinterability and parameters of pure B₆O materials consolidated by using reactive and non-reactive spark plasma sintering of B₆O and B₂O₃/B powders.

EXPERIMENTAL METHODS

Precursors were prepared by mixing amorphous boron (97.8%) with water solution of B₂O₃ at various ratio of the components followed by evaporation of water, drying and milling. The obtained powder with specific surface area of 17 m²/g was used for reactive sintering.

The B₆O for non-reactive sintering was prepared by calcination of B/B₂O₃ precursor at 1400 °C for 1 h [2]. The prepared samples were pressed into graphite dies with diameter of 20 mm and densified in vacuum at 1600–1900 °C and pressure of 30 MPa using SPS-825.CE (SPS Syntex Inc.). The sintered bodies were polished to remove admixture of graphite and B₄C.

RESULTS AND DISCUSSION

Densification of B₆O samples started at 1540 °C and highest relative density of bulk material (98%) were reached at 1900 °C during 5 min.

Reactive spark plasma sintering of the B/B₂O₃ started at 520 °C and final density

was reached at temperature of 1800 °C during 5 min.

The increase of holding time or temperature up to 1900 °C accelerated only grains growth. The both sintered samples contained crystalline B₆O. Obviously, the deposition of B₂O₃ on the surface of the boron leading to obtaining uniform mixture promoted formation of B₆O.

The reactive sintered sample consisted from irregular grains with size of 1.5–4.0 μm but crystallite of sintered B₆O was in the range of 18–40 nm. It indicated that grains involved many crystallites. Microstructure of non-reactive sintered samples showed plate-like grains and crystallite size was in the range of 30–45 nm. From results followed that relatively simple reactive sintering of B/B₂O₃ mixture of molar ratio B/B₂O₃=14 accelerated densification process and ensured preparation of B₆O materials at lower temperature.

CONCLUSION

The use of reactive spark plasma sintering of B/B₂O₃ at molar ratio of 14 simplified preparation technique of B₆O manufacturing with relative density about 97% at 1800 °C during 5 min with respect to non-reactive sintering of B₆O powder.

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Spark Plasma Sintered WC-Fe Hardmetals

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INTRODUCTION

Traditionally Co is preferred binder metal in WC hardmetals due to very good wetting with WC, notable solubility of WC in cobalt and excellent strength and ductility of WC-Co composite [1]. In recent decades, the high price, limited availability and health concerns of Co have been motivation to study other transition metals (Ni, Fe, Cr) as alternative to replace Co. Fe and Fe alloys are promising candidates and they are already employed in specific applications [2]. This work focuses on Spark plasma sintered (SPS) WC-Fe Hardmetals.

EXPERIMENTAL METHODS

Conventional milling in ball mill with hardmetal balls was utilized to prepare WC-Fe powders. Compaction was carried out with SPS furnace HP D 10-GB from FCT Systeme GmbH. Sintering parameters are exhibited in table 1. WC-Co hardmetal was prepared as reference material using same production method. Hardmetal specimens were characterized by means of hardness, fracture toughness and SEM images of microstructure.

Table 1. Prepared materials and sintering parameters

Sample	Material	Sintering parameters
W1	WC – 15wt.% Fe	temp. 1200 °C, 5 min; pressure 50 MPa;
W2	WC – 15wt.% Co	temp. ramp rate 100 °C/min,

RESULTS AND DISCUSSION

Spark plasma sintered hardmetals with Fe binder exhibit higher hardness and lower fracture toughness when compared with WC-Co. Noteworthy extra hard layer forms on the surface of WC-Fe specimens. The layer thickness is around 0.5 mm and hardness increase is around 300 Vickers hardness units when compared to the sample core (1750 vs 1450 HV10). The formation of surface layer can be attributed to the

carbon pick-up from surrounding graphite mold during sintering. Microstructure of WC-Fe is fine grained and contains traces of η -phase.

CONCLUSION

WC-Fe and WC-Co materials were prepared by conventional ball milling followed by SPS. Fe binder exhibited higher hardness and lower toughness as well as formation of extra hard surface layer.

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ACKNOWLEDGMENTS

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Technological Peculiarities of TiC-FeCrMn Cermet

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INTRODUCTION

The most widespread TiC- and TiCN-based cermets are bonded with Ni-Mo alloys [1]. But nickel is known as an allergen and toxic for human health. Therefore, several alternative binders have been investigated [2]. Previous research has proved possibility to produce TiC-based cermets bonded with Ni-free stainless steel [3]. Even though manganese have been used to stabilize the austenitic phase, using manganese has a couple of drawbacks: high affinity of oxygen and high vapor pressure.

EXPERIMENTAL METHODS

TiC-based cermets have been produced using PM technology. TiC, ferritic stainless steel AISI 430L and elemental manganese powders have been used. The powders were ball-milled, uniaxial pressed and liquid-phase sintered using three different partial pressure levels: vacuum 4 Pa; argon partial pressure 400 Pa and 40 kPa. Fracture toughness and hardness were determined. Chemical composition of cermets after sintering was analyzed using X-ray spectroscopy.

RESULTS AND DISCUSSION

Calculated chemical composition is presented in Table 1.

Table 1. Calculated chemical composition of 70TiC-FeCr14Mn20 cermets

Grade	TiC, wt%	Binder composition, wt%		
		Cr	Mn	Fe
1	30	13.6	6.0	Bal.

Also all cermets have acceptable mechanical properties and sinterability (see Table 2).

Table 2. Mechanical characteristics of 70TiC-FeCr14Mn20 cermets sintered using partial pressure of argon (40 kPa)

Grade	Hardness, HV30	Fracture toughness, MPa·m ^{1/2}	Porosity, %
1	1244	9.6	0.57

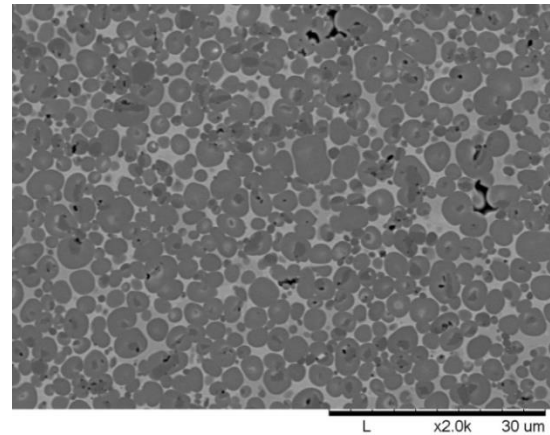


Fig.1. Microstructure of cermet 70TiC-FeCr14Mn20

CONCLUSION

Ni-free TiC-based CrMn-steels bonded cermets demonstrates good sinterability and acceptable mechanical characteristics. The microstructure is quite homogenous (see Fig. 1). Depression of manganese evaporation can be achieved using partial argon pressure during sintering.

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Properties of Nanosized Ferrite Powders and Sintered Materials Prepared by the Co-precipitation Technology, Combined with the Spray-drying Method

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INTRODUCTION

Ferrite nanoparticles are widely applied in life sciences, biochemical processes and special coatings. Several liquid and gas phase synthesis have been developed to synthesize ferrite nanoparticles. One of these is the co-precipitation method [1]. Main disadvantage of this is difficult and slow precipitation stage of obtained hydroxides.

In this research the co-precipitation synthesis is combined with the treatment of the obtained suspension by the spray-drying method with the following thermal treatment of granules, and structure and magnetic properties of these ferrites have been studied.

EXPERIMENTAL METHODS

Synthesis of Ni and Co ferrite nanoparticles were performed by the co-precipitation technology [2], combined with the spray-drying of the hydroxide mixture suspension at 120-130 °C and thermal treatment at different (350-950 °C) temperatures. Reagent grade chemicals were used: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, urea, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaOH.

Samples were pressed (200 MPa) in pellets with 12 mm diameter, height 4 - 6 mm, and sintered for 2 h isothermally in air at 1000-1300 °C (10 °C/min) in the furnace LHT-08/18 (Nabertherm GmbH).

Samples were analyzed by the X-ray diffractometer Advance 8 (Bruker AXS), crystallite size find by the Scherrer's equation, magnetic properties - by vibrating sample magnetometry (VSM Lake Shore Cryotronics, Inc., model 7404 VSM), specific surface area (SSA) - by the BET single point method. The size and morphology of particles as well as the microstructure of the sintered materials were observed by SEM (Mira/Tescan).

RESULTS AND DISCUSSION

Granules of size to 5 μm (Fig. 1.) and average particle size of 10-15 nm were obtained. Starting from 350 °C, the single phase product (NiFe_2O_4 or CoFe_2O_4) with the SSA from 100 (at 350 °C) to 20 m^2/g (at 950 °C) was obtained. The magnetic saturation (M_s) of NiFe_2O_4 and CoFe_2O_4 rises from 6 and 15 emu/g (at 450 °C) to 40 and 77 emu/g (at 950 °C), resp.

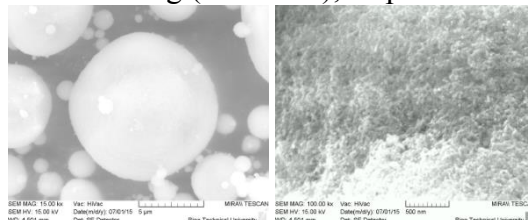


Fig. 1 The electron microscope image of spray-dried NiFe_2O_4 at different enlargements

Density of samples sintered at 1100 and 1300 °C increases from 90% to 95% for CoFe_2O_4 and from 82% to 94% for NiFe_2O_4 . M_s at 1300 °C reaches 44 and 79 emu/g , resp. for NiFe_2O_4 and CoFe_2O_4 .

CONCLUSION

Single phase Ni and Co ferrite nanopowders were successfully synthesized by the modified co-precipitation synthesis method. The average particle size of obtained nanopowders is in the range of 15-50 nm, depending on thermal treatment temperature (TTT). Magnetic saturation values of them depend on TTT (6-40 emu/g for NiFe_2O_4 , 15-77 emu/g for NiFe_2O_4). Rather dense material by the pressure-less sintering forms at 1100 °C for CoFe_2O_4 and 1200-1300 °C for NiFe_2O_4 .

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Sintering of Fe-ZrO₂ composite powders by a thermochemical synthesis

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INTRODUCTION

Oxide dispersion - strengthened (ODS) materials are of the great interest because of their high strength especially at elevated temperatures. The main target in technology of ODS materials production is to achieve a homogenous distribution of fine oxide particles in metal matrix [1]. This work presents a method obtaining of the iron-based material reinforced with zirconium oxide by spray drying of salts water solution with subsequent reduction heat treatment.

EXPERIMENTAL METHODS

The required amount of iron nitrate and zirconyl nitrate were soluted in a distilled water. The solution was spray dried at 150°C on Buchi Spray DryerB-290 to produce the precursor powder. Then the precursor powder was heated at 700°C in air with formation of the oxides mixture. The obtained oxide powders were heat treated in a hydrogen atmosphere at a temperature of 800°C for 1 hours, whereby the iron oxide was reduced and the ZrO₂ remained unchanged. The morphology and size of the particles were observed by scanning electron microscopy on MIRA 3 TESCAN, phase composition was analyzed by XRD on X-ray diffractometer DRON-2 using CuK- α monochromatic radiation. Temperatures of phase transformations have been determined by DTA at heating of 10°/min.

RESULTS AND DISCUSSION

Because of low content of Zr there are only α -Fe reflects observed by XRD analysis of the synthesized powders. In order to find phase containing Zr the powder was treated with 15% hydrochloric acid to dissolve the iron particles. The residue, as found by XRD (Fig.1,a), is ZrO₂. The size of the particles is less than 70 nm (Fig.1,b). An effect of heat treatment on the size and morphology of the zirconium oxide particles have been investigated. Fig.1,b

shows the microphotographs of the ZrO₂ annealed at 1030 °C.

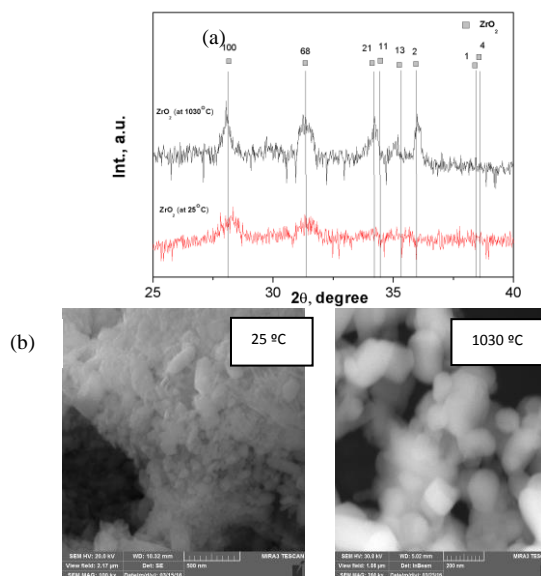


Fig.1. X-ray diffraction (a) and SEM (b) results of a zirconium oxide as-synthesized and annealed at 1030 °C state

CONCLUSION

The Fe-1% ZrO₂ nanocomposite has been synthesized by thermochemical methods using spray dry technique and subsequent heat treatment. The powder has been characterized with SEM, DTA and XRD analyses. The proposed method allowed to produce a composite powder Fe-1% ZrO₂ with homogeneous distribution of nanosize zirconium oxide in the iron matrix.

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Fabric Finishing with Flame Retardant Coating

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INTRODUCTION

Due to its wide application improvement of fire protection of materials has always been topical. Aim of the research is to render textile materials less flammable in an economically and environmentally friendly manner.

Examples of FR coated fabrics are furniture upholstery, roller blinds, interior materials for transportation, protection garments etc. [1,2]. Products testing are carried out to ensure customer satisfaction and differ for materials of various kinds. In the case of coated fabric the abrasion resistance tests is required. Flame retardency standarts for public safety are generally controlled or influenced by government departaments, taking into account environmental restrictions.

EXPERIMENTAL METHODS

Plain weave bleached cotton fabric was used for experiments. Influence of cyclic phosphonate flame retardant Itoflam PES (producer LJ SPECIALITIES LTD) with alkaline agent NH₄OH addition on substrate flammability was investigated. Exhaustion method from water solutions was used for treatment. Conditions: Liquor ratio 30, concentration of Itoflam PES 60, 100, 140 g/L, concentration of alkaline agents 20% and 25%. Drying at 120 °C for 2 min, thermal treating at 180 °C for 1 min.

The flat screen coating method was used for additional treatment of cotton fabric with commercial printing pastes (producer CHT BEZEMA) Printperfect LAC 60, Tubiscreen EX-TS and Printperfect EX-AR with additive antimony trioxide (Sb₂O₃). Drying at 100 °C for 7 min, thermal treating at 150 °C for 5 min.

The adapted LVS EN ISO 15025:2003 horizontal method for flammability tests was used. Coated textiles were examined from right and left sides. Tensile strength/elongation properties of samples according LVS EN ISO 13934 – 1: 1999 on device Instron 3345, abrasion resistance

with Taber abrasion method as faster one [1] on Taber Rotary Platform abraser, according LVS EN ISO 5470-1:2001 and the stiffness properties with Shirley tester according recommendations of device were tested.

RESULTS AND DISCUSSION

Treatment with Itoflam PES reduces cotton's reaction to fire. Examination of kind of alkaline agent and concentration influence shows that optimal composition is Itoflam PES 140 g/L water solution with 25% NH₄OH addition. Further the fabric was coated with different thickness layers on base of commercial printing compositions. As such materials are often used in blinds, materials for transportation and others, the tensile strength/elongation properties and stiffness properties were tested.

CONCLUSION

Fabric impregnated with Itoflam PES with extra fireproofing coating reduces cotton's reaction to fire. The resulting effect varies with the type and composition of coating. Thickness of coating has little impact on cotton's fire reaction readings. The best fire suppression for non foam coating is achieved by paste Printperfect LAC 60, but for foam coating – paste Printperfect EX-AR. Coatings cause slight increase of tensile strength and decrease of relative elongation. Paste Tubiscreen EX-TS provides the greatest friction resistance, amounting to 3856 abrasion cycles. Foam finishing have higher abrasion resistance than non foam coatings.

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Comparative Analysis of Methods for Evaluating Wear Rate of Nanocrystalline Diamond Films

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INTRODUCTION

The study deals with the wear of nanocrystalline diamond (NCD) films. Various adaptation processes were observed between contacting surfaces in our previous studies [1, 2], which include asperity polishing, formation of carbonaceous tribolayer and ripple patterns on the wear scar surfaces, and deflection of the diamond films. Due to the effect of film deflection the apparent wear volume can differ from the volume of the removed material. Therefore, evaluation of different methods for the calculation of the wear of diamond films is the focus of the present study.

EXPERIMENTAL METHODS

NCD films were grown on (100)-oriented Si wafer by microwave plasma enhanced chemical vapor deposition (MWPCVD) method in CH₄/H₂/air plasma. The tribological properties were tested under reciprocating sliding test conditions using Si₃N₄ balls. Wear scars were investigated by means of mechanical profilometry and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

The wear rates with corresponding uncertainties were evaluated using the depth profiles of the wear scars and the SEM cross-sections taken within the wear scars, see Fig.1. The main sources of uncertainties were estimated.

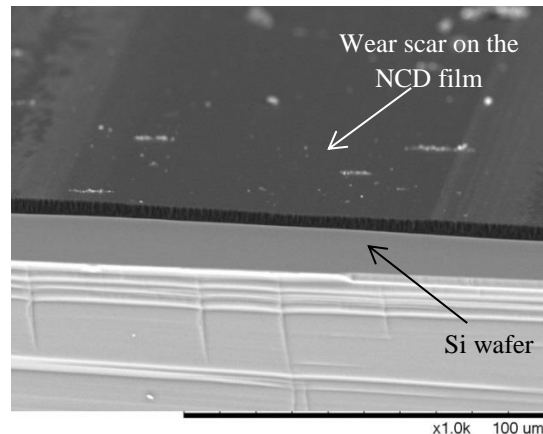


Fig.1. SEM cross-section of the NCD film taken across the wear scar

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ACKNOWLEDGMENTS

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Effect of sintering method on surface fatigue of carbide composites

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INTRODUCTION

In this work the influence of sintering method on the surface fatigue of carbide composites was studied. The research focuses on WC-based composites (hardmetals), TiC – and Cr₃C₂ – based cermets sintered using different techniques and as a result different microstructure: regular vacuum sintering; compression sintering (sinterhipping); reactive sintering and spark plasma sintering (SPS method).

EXPERIMENTAL METHODS

Materials, testing and materials characterization was performed using testing facilities of the Tallinn University of Technology (TUT). Surface fatigue testing complemented by microstructure investigations using optical and scanning electron microscopy.

RESULTS AND DISCUSSION

The typical surface fatigue degradation mechanism [1] - binder extrusion and large grains pull-out continuing with crushing of binderless grains - was observed for all studied materials. The titanium carbide based nickel-molybdenum bonded cermets show advantage in surface fatigue resistance and sensitivity if compared to other tested carbide composites. Testing analysis revealed no correlation between hardness, fracture toughness and surface fatigue behavior of tested materials.

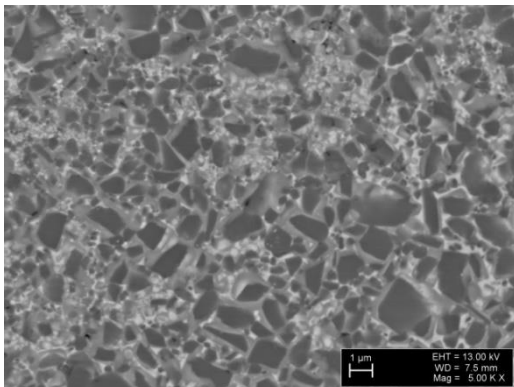


Fig.1. Microstructure of TiC-30wt%NiMo cermet

The examples of the microstructures of some studied materials are shown in Figs. 1 and 2. The carbide composites compositions there selected to be of similar average grain size range.

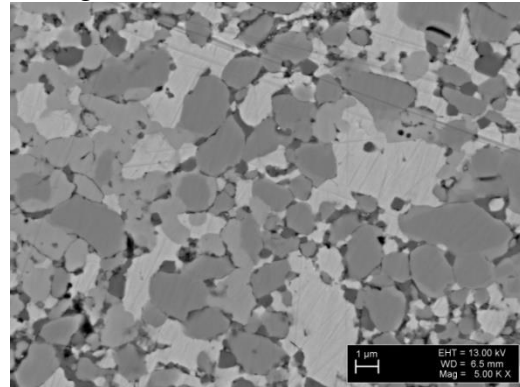


Fig.2. Microstructure of Cr₃C₂-30wt%Ni cermet

CONCLUSION

Composites sintered by conventional vacuum sintering method have an advantage to withstand cyclic impact loads over those prepared using reactive sintering. The reason could be the higher porosity of latter revealed by microstructural analysis.

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Contact Estimation Using 3D Surface Roughness Parameters

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INTRODUCTION

The key purpose of this work is to propose a methodology of contact prediction of wear parts using 3D surface roughness parameters defined in the standard ISO 25178 part2 for friction and wear rate determination. In our research the random surface model was used, where the height of surface asperities $h(x,y)$ has a normal probability distribution. As a result of research the equations for estimation of the elastic contact area and friction coefficient were derived. The correlation between friction coefficient and 3D surface roughness parameters exist as well. The results of this work have wide practical application, for example in design, the texture specification on drawings, calculation of load, etc.

CONTACT AREA DETERMINATION

The contact problem of an elastic sphere with the plane is solved in the classical theory of elasticity without considering the roughness of real bodies in mechanical engineering. The problem of contacting taking into account the roughness problem examined in the research [1]. However these numerical methods do not give a analytical expressions for calculating real contact area and also closer contact details of bodies by friction. In our research the random surface model was used. The surface machined by abrasive instruments (grinding, polishing, honing etc.) has the irregular surface texture, which can be described by random function. Irregular surface is expressed by random field $h(x,y)$ of two variables x and y which are cartesian coordinates of surface point, where the height of surface asperity $h(x,y)$ has a normal probability distribution.

$$\xi(x,y) = h(x,y) + f(x,y)$$

where:

$h(x,y)$ - normal stationary random field

$f(x,y)$ - nonrandom function of two variables (the scope of the equation in the selected reference system).

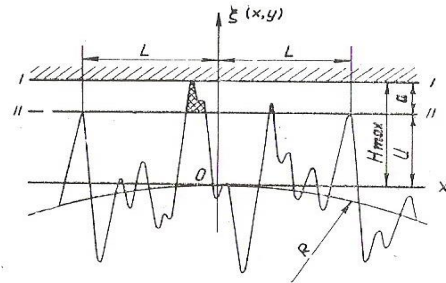


Fig.1. Calculation scheme

EXPERIMENTAL METHODS

The example of friction coefficient prediction is get for face surface of a pin-on-disk in the case of

elastic contact. Parameters of microgeometry of pin surface were measured by "Taylor Hobson Intra50". 3D measurements with stylus instrument were achieved by basic "stepping" method and data processing by computer.

CONCLUSION

At a first time the 3D surface roughness parameters in the formulas for contact area and friction coefficient were used. It was revealed that the correlation between friction coefficient, contact area and surface roughness parameters exist. Also we get that surface roughness give greater influence to contact area at lower load.

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Electrodeposition of Cobalt and Lead in the Hybrid Liquid Membrane – Electrodialysis – Electrolysis Process

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INTRODUCTION

The removal of toxic Co(II) and Pb(II) ions from effluents and waste waters is a problem of great significance. Liquid membrane technology has great potential for the removal of heavy metals from aqueous dilute solutions [1]. Application of a direct electric field significantly intensifies the transport of ions through the liquid membranes [2]. Di(2-ethylhexyl)phosphoric acid (D2EHPA) is an important acidic extractant in hydrometallurgy. The aim of the present work is to study the membrane extraction of Co(II) and Pb(II) by D2EHPA – based bulk liquid membranes with electrodeposition of metals in the cathodic solution during a galvanostatic electrodialysis – electrolysis process.

EXPERIMENTAL METHOD

The experiments were carried out in the system:

(+) Pt	Feed	Liquid	Pt (-)
Anolyte	solution	membrane	HClO ₄

The solutions of D2EHPA with the admixtures of tri-n-octylamine in 1,2-dichloroethane were used as the liquid membranes. They contained usually 20 vol.% D2EHPA and 0.1 M TOA. The liquid membrane was separated from the aqueous solutions by two cellophane films. The feed solution contained 0.01 M CoSO₄ in 0.01 M H₂SO₄ or 0.01 M Pb(NO₃)₂ in 0.01 M HNO₃. Anolyte containing H₂SO₄ or HNO₃ solution was separated by the solid anion exchange membrane MA-40 or cation exchange membrane MK-40. The direct electric current was supplied to the plane platinum electrodes.

RESULTS AND DISCUSSION

It has been found out that the imposition of an electric field allows to extract Co²⁺ cations from H₂SO₄ solution as well as Pb²⁺ cations from the HNO₃ solution through the liquid membrane and obtain cathodic cobalt electrodeposits from HClO₄, HNO₃, HCl,

H₂SO₄ solutions and lead coatings from HClO₄ and HNO₃ solutions. Compact, adherent cobalt and lead electrodeposits of fine-grained structure are obtained from dilute HClO₄ solutions (Fig.1.).

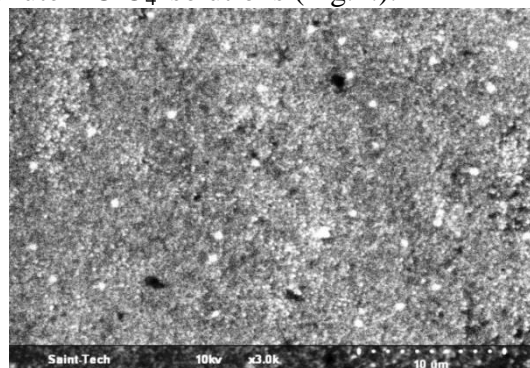


Fig.1. Scanning electron microscopy image of the cobalt coating deposited from 2,5·10⁻² M HClO₄.

The increase of the current density as well as of the metal initial concentration in the feed solution results in the increase of the Co(II) and Pb(II) transport and electrodeposition rates. The practically complete removal of Co(II) (>99%) and Pb(II) (98%) from the feed solution is achieved in the studied systems. The increase of the acid concentration in the feed solution and HClO₄ concentration in the catholyte negatively affects the membrane extraction process.

CONCLUSION

The electrodialysis through the liquid membranes is a feasible technique for the removal and electrodeposition of Co(II) and Pb(II) cations from dilute solutions.

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Fe₂O₃-TiO₂ coating structure and hydrophobicity

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INTRODUCTION

The imperative environmental need to eliminate pollutants makes the search for new catalyst materials with improved properties and efficiency. Heterogeneous semiconductor photocatalysis is a popular technique that possesses great potential to control air pollutants and aqueous organic contaminants [1-2].

EXPERIMENTAL METHODS

The crystalline phases formed during thermal treatment of xerogels were determined using X-ray analysis. The surface morphological investigation of the coatings was performed with a scanning electron and atomic force microscopes. Coating optical properties were investigated using UV/VIS spectrophotometer. Wettability of sample surface was evaluated depending on the deposition speed and distilled water content in TiO₂-Fe₂O₃ sol-gel solution.

RESULTS AND DISCUSSION

After annealing at 500 °C, the agglomeration of iron oxide and titanium atoms on the film surface resulted in formation of leaf-like structures with the size of 50–200 nm. SEM micrographs of leaf-like Fe₂O₃-TiO₂ film structure on glass slide substrate with 65 mol% Fe₂O₃ ratio are shown in Fig. 1a and 1b. AFM images of the deposited Fe₂O₃-TiO₂ thin film (with thickness of 300 nm) shown in Fig.1c.

Figure 2 shows the hydrophobic properties of TiO₂-Fe₂O₃ films on glass substrates. As shown in Fig.2. the coating preparation, deposition speed and heat treatment time affects the surface and the properties of coating, including wettability angle. The contact angle of water droplets on film surface reaches up to 112° (after 7 days). After heat treatment the contact angle is under 30° due to a lack of hydroxyl groups on a sample surface.

Coated sample XRD peaks shows formation of hematite and anatase crystalline phases. No considerable peaks related to Fe-Ti composition phases were observed in the pattern.

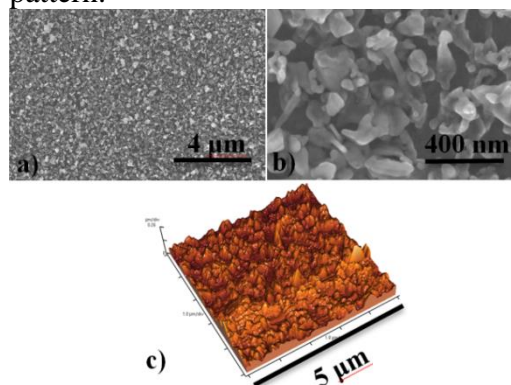


Fig.1. SEM image of the sample surface a) and b), 3D AFM image of the surface c)

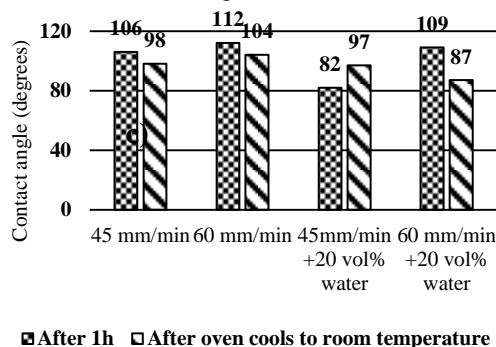


Fig.2. Contact angle of TiO₂-Fe₂O₃ coatings prepared changing film deposition speed and adding 20 vol% distilled water

CONCLUSION

Leaf-like structure TiO₂-Fe₂O₃ thin films with the sizes from 50 to 200 nm were fabricated by sol-gel dip coating process. Thin coatings with high Fe₂O₃ content (65 mol %) shows wettability angle of 110°.

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Tribological Properties of Zirconium Oxide, Spinel and Mullite Nanopowders as Lubricating Oil Additives

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INTRODUCTION

In work investigated effects of zirconium oxide (ZrO_2), spinel (MgAl_2O_4) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) nanosized powders on the base oil tribological properties. The nanosized (30-40nm) powders manufactured by plasma chemical synthesis method. Tribological experiments used on ball-on-disc type tribometer, measured coefficient of friction and determined metallic disc wear. Base oil used selectively purified mineral oil without any functional additives. Nanosized powders dispersed in base oil at 0.5; 1.0; 2.0; wt.%. At work concluded, that the addition nanoparticles in base oil, possible reduced friction pair wear and friction coefficient. As the main results include spinel (MgAl_2O_4) nanoparticles 0.5 and 1.0 wt. % concentration ability reduced friction coefficient value.

MATERIALS AND METHODS

Materials characterization

The nanosized powders were manufactured by plasma technology developed in the Institute of Inorganic Chemistry of the Riga technical University. The experimental equipment and procedure more detailed is described in [1]. In experiments will be used selectively purified industrial mineral oil I-40, that is free of any additives, in order to exclude the impact of other additives. As well were prepared, nanoparticle compositions with base oil, ceramic powder nanoparticles dispersed in oil at 0,5; 1,0; 2,0 wt% concentrations.

Experimental conditions

The present slip friction experiments were carried out using the ball-on-disc tribometer, following scheme (see Fig.1), where the disk is metallic sample, which is rotating, but the ball is a stationary tribometer element. This method complies with ASTM G-99 and DIN 50324 - "Tribology; testing

of friction and wear model test for sliding friction of solids".

The ball-on-disc tests were performed under force 20 N with a sliding distance of 56,55 m, linear velocity 0.1 m/s (at 3 mm radius from the center of disc), measurement time 550 s includes 3000 rotational cycles. Material of the ball 100Cr6 (ISO:630-17), diameter of the ball 6 mm, material of disc sample Steel S235 (ISO:683-2).

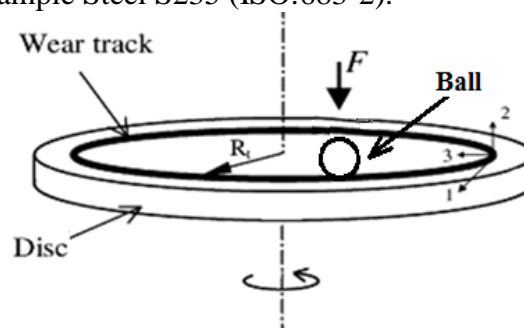


Fig.1. "Ball on disc" test scheme

CONCLUSION

These investigation tribological tests show, if modificate base oil with nanoparticles, possible improve friction pair tribological properties. As the main results include spinel (MgAl_2O_4) nanoparticles 0.5 and 1.0 wt% concentration, ability reduced friction coefficient value until 12%, compared with base oil at these tribological test conditions.

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Compatibilizers effect on Silyl-terminated polyether/ Epoxy resin system mechanical and rheological properties

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INTRODUCTION

In this work we study influence of compatibilizers on tensile and rheological properties of new Silyl terminated polymer/Epoxy two component systems. In early works about that kind of systems most of attention was devoted to polymers used (mainly silyl terminated polyether), while less attention was paid to justification of the choice of catalysts, compatibilizers and additives [1-2]. One of the most important system elements are compatibilizers, while in this particular system silyl terminated polyether cannot react with epoxy groups directly. This work indicates that compatibilizer has a crucial meaning on materials mechanical properties.

EXPERIMENTAL METHODS

Silyl terminated polymer (SAX 520) was mixed with epoxy resin (D.E.R. 331) at various weight proportions starting from 60/40 until 30/70, respectively. Compatibilizers - 3-Glycidyloxypropyltrimethoxysilane (*es*) and N-(n-Butyl)-3-aminopropyltrimethoxysilane (*sam*) - were added at constant weight (1.5 g) in every series blend and compared with series without compatibilizer. Blends were mixed using SpeedMixer DAC 150 centrifugal laboratory mixer, casted in Teflon moulds and cured at standard conditions (23±2 °C, 50±5% RH) for 1, 7 and 28 days.

Rheological measurements were tested by using Bohlin CVO 100 rheometer. Instrument was equipped with 20 mm diameter spindle with plate-plate geometry (gap size 1000 µm). Tests at 25 °C were performed in oscillation mode – frequency 1 Hz and strain 0.006.

Tensile stress-strain measurements were performed by using Zwick /Roell Z010 universal testing machine. Tests were made

according to GOST 21751-76 at test speed 100 mm/min.

RESULTS AND DISCUSSION

In Table 1 we can see how silane compatibilizers influence two component system mechanical properties. 50 to 50 SAX 520/D.E.R. 331 ratio has been established as the most efficient to develop two-component systems with enhanced performance. Table below show tensile strength and Shore A values with and without compatibilizers for SAX 520/D.E.R. 331 ratio of 50/50.

	1 day		7 day		28 days	
	σ_B MPa	Shore A	σ_B MPa	Shore A	σ_B MPa	Shore A
<i>Standart</i>	0.77	25	0.97	31	1.69	38
<i>es</i>	0.89	28	1.54	30	2.21	38
<i>sam</i>	2.44	32	4.53	38	6.18	47

As one can see use of *sam* type silane provides considerably better mechanical properties than use of *es*.

CONCLUSION

Compatibilizers cause different effects on two component Silyl terminated polymer/Epoxy resin system. Influence of silane *es* on mechanical properties of SAX 520/D.E.R. system is relatively negligible, whereas addition of *sam* increases material tensile strength and Shore A value 3.65 and 1.2 times, respectively.

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Hardening of Steel Perforated Tape by Nd:YAG Laser

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INTRODUCTION

Perforated metal materials (PMM) have wide application in the manufacture of products from small and medium-carbon steels. One of the new areas of PMM application can be their use as cutting elements in the manufacture of machining tools [1]. In this case it is necessary to carry out strengthening of cutting surfaces to increase their hardness.

One method may be laser processing, which in contrast to the known processes of heat strengthening (bulk quenching of high-frequency currents, electric heating and etc) is not bulk but the local, superficial process, without change of surface both macro and microgeometry [2]. In the present work the effect of laser exposure modes on the microstructure and hardness of steel perforated tape has been investigated.

EXPERIMENTAL METHODS

The St50 steel samples from perforated tape 1.2 mm thick (Fig.1.) were irradiated by pulsed Nd:YAG laser with following parameters: $\lambda=1064nm$, $\tau=6\text{ ns}$, $I=104.2MW/cm^2$. Different scan speeds (doses) were used in the experiments. Hardness by methods of micro- and nanoindentation and microstructure of the surface layers were investigated.



Fig.1. View of PMM

RESULTS AND DISCUSSION

Investigations showed that after the laser treatment the microhardness increase from 1.68 to 2.50 GPa is observed in the surface layer of 1 μ m. Moreover, according

nanoindentation in the layer of 0.1 μ m hardness increases to 5 GPa, with a small decrease in Young's modulus from 190 GPa to 210 GPa.

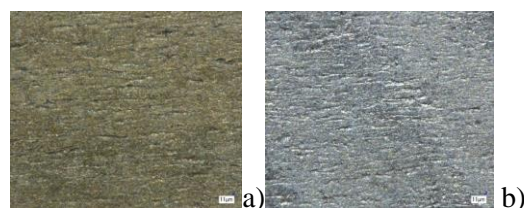


Fig.2. Micrographs of St50 samples (a) non-irradiated and (b) irradiated by Nd:YAG laser

Microstructure studies have shown refinement of the ferrite and pearlite structures in steel and the presence of a thin oxide films on the surface. Last is consistent with the results of nanoindentation. It should be noted that hardening of the laser beam was performed without melting of the surface that excludes both the macro roughness change and the need for subsequent machining.

CONCLUSION

The work shows that laser treatment leads to the hardness increase by 66% in surface layer of 0.1 μ m and by 48% in layer of 1 μ m. The effect falls off at a depth of 2 μ m. Changes in the microstructure with conservation of surface macrorelief are detected. The mechanisms of laser action processes and ways of possible applications of the new material are discussed.

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On the tribological behaviour of different hot-dip aluminised steels

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INTRODUCTION

Hot dip aluminising of steels is applied to enhance surface properties such as corrosion resistance and surface hardness due to the formation of iron aluminide layers [1], which can improved wear resistance [2]. Processing parameters (bath temperature and immersion time) and the chemical composition of the steel strongly influence the formation of aluminide layers. In this study wear properties of aluminide layers were investigated at different iron based alloys. The wear resistance of the various layers was investigated by scratch testing. Layer thickness, the hardness and present iron aluminide phases causes changes in the wear mechanisms.

EXPERIMENTAL AND ANALYSIS

Hot dip aluminising was performed in a laboratory furnace at 700 °C in a pure aluminium melt for 1, 5 and 8 h. Three different iron based alloys were chosen for investigation: i) pure iron, ii) austenitic steel 1.4301 and iii) white cast iron 1.4777. Metallographic samples were examined via SEM/EDX regarding aluminide phases and their layer thickness. For the scratch tests, remaining aluminium process was removed, followed by a fine grinding process. Scratch tests were performed using a TriboTest® scratch tester with a Rockwell C diamond tip. The loading range was set from 1-100 N to identify critical loads leading to layer failure. The, normalised to the layer thickness, critical pressure p_{crit} is calculated as:

$$p_{crit} = \frac{F}{A_{sc}} = \frac{F}{\pi \cdot r \cdot d \cdot h} \left[\frac{N}{mm^3} \right] \quad (1)$$

where F is the critical failure force, r the radius of the indenter, h the indented depth and d the scale thickness. After scratching, further metallographic, topographic and SEM investigations were performed.

RESULTS AND DISCUSSION

After scratch testing the scratch depth was measured and critical pressures were calculated via layer depth, which can be seen in Fig.1.

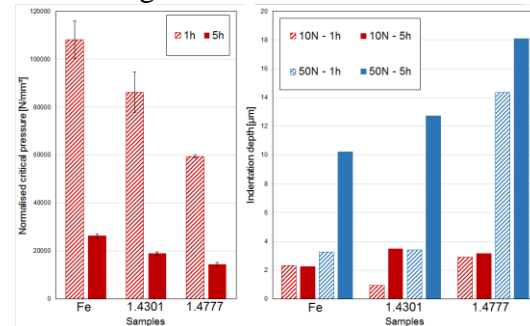


Fig.1. Indentation depths and normalized critical pressures of all materials tested

As seen in the figure, critical loads and indentation depths strongly depend on the base material and therefore on the chemical composition of the aluminides. Wear mechanisms analysed with SEM, point out, that pure iron aluminides are the hardest, but behave brittle exceeding critical loads, while both 1.4777 and 1.4301 incorporates pure Al, which increases ductility and deformation within worn zones. Generally can be said, that base material, dipping time, layer thickness and formation cause strongly influences the scratch and wear behaviour.

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ACKNOWLEDGMENTS

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