

Basic research 2010

Title of the achievement: Development of PTZ thin films microstructure prepared by modified sol-gel method.

Pb(Zr_{0.52}Ti_{0.48})O₃ (PZT) thin films were prepared by a modified sol-gel method of precursors (sols) and their deposition using spin-coating method onto Pt/Al₂O₃ a Pt/SiO₂/Si substrates. Results of XRD analysis confirmed that the transformation of the amorphous PZT film to perovskite structure happened after sintering at 650°C. The mechanism of microstructure formation has described for morphologically different perovskite particle types in 1, 2 and 3-layered PZT thin films with thickness of 200-500 nm on used substrates. Three different PZT film microstructure types with columnar structure on film cross-section in dependence on the applied sol concentration (0.5-1.5M) were confirmed. It was found that the PZT/Pt/Al₂O₃ film microstructures at 1.0M sol concentration were composed of two forms of perovskite particles, big rosette (~ 1-5 μm) and irregular cuboidal particles (~ 0.5-1.5 μm). Contrary to above facts, a strong different microstructures of the PZT/Pt/Si/SiO₂ film, which contained small spherical particles with size of (~ 40-100 nm) and (~ 0.2-1.0 μm) and rosettes composed of small cuboidal particles (~50-120 nm), were observed.

BRUNCKOVÁ, H. - MEDVECKÝ, Ľ.: Effect of sol concentration and substrate type on microstructure formation of PZT thin films. *Ceramics-Silikaty*, accepted D-10-00048R1, 2010. ADCA

BRUNCKOVÁ, H. - MEDVECKÝ, Ľ.: Effect of sol concentration and substrate type on microstructure formation of PZT thin films. *Ceramics-Silikaty* in print D-10-00048R1, 2010

BRUNCKOVÁ, H. - MEDVECKÝ, Ľ.: Effect of sol-gel preparation method on particle morphology in pure and nanocomposite PZT thin films. *Chemical papers CHP- 409-10*, submitted

BRUNCKOVÁ, H. - MEDVECKÝ, Ľ. - HVIŽDOŠ, - P ĎURIŠIN, J.: Effect of composite PZT thin films preparation by sol-gel method on their morphology and nanohardness. Conference, *Lokálne mechanické vlastnostiLMV 2010*, Smolenice, 10.-12.11.2010. *Chemické listy*, submitted

AFDA-Publ. prís. na medz. konf. v SR

BRUNCKOVÁ, H. - MEDVECKÝ, Ľ. - ĎURIŠIN, J.: Influence of substrate on the microstructure thin PZT films prepared by spin-coating method from sol-gel precursors. *Acta Metallurgica Slovaca Conference*, 2010, no. 2, p.120-124

Title of the achievement: The study of the creep behaviour and thermal shock resistance of Si₃N₄-SiC composites with rare-earth oxide additives

VEGA 2/0156/10: The study of the creep behaviour and thermal shock resistance of Si₃N₄-SiC composites with rare-earth oxide additives, *principal investigator: Mgr. Monika Kašiarová, PhD.*

Nanosmart Centre of Excellence of SAS, *principal investigator: Prof. RNDr. Ján Dusza, DrSc.*

Influence of various rare-earth oxide additives (La₂O₃, Nd₂O₃, Sm₂O₃, Y₂O₃, Yb₂O₃ and Lu₂O₃) on the microstructure and mechanical properties of the Si₃N₄-SiC micro/nano-composites (developed at IICH SAS Bratislava) has been investigated. These results were consequently compared to those obtained on the reference monolithic Si₃N₄ with the same sintering additives. The sintering additives and the processing routes result in bimodal microstructures of silicon nitride as well as Si₃N₄-SiC composites with elongated β-Si₃N₄ grains embedded in fine grained Si₃N₄ matrix. The aspect ratio of β-Si₃N₄ grains slightly increased with a decreasing ionic radius of rare-earth element. The fracture toughness of composites as well as monoliths slightly increased with a decreasing ionic radius of RE³⁺. The ceramics sintered with the addition of smaller rare-earth cation (e.g. La³⁺, Nd³⁺) exhibited toughening mechanisms more frequently compared to the ceramics with larger ones (Lu³⁺). The materials sintered with the additives with smaller radius of RE³⁺ exhibited the higher values of mean bending strength. The friction coefficient decreased with a decreasing ionic radius of the rare-earth element in both the monoliths and the composites and the SiC particles seem to be effective in reducing the friction coefficients of Si₃N₄ based materials as well. The specific wear rate significantly decreased with a decreasing ionic radius of rare-earths in both the monolithic and the composite material caused by the positive effect of the smaller ionic radius of RE on the bonding strength between grains and intergranular phase. Higher bonding strength restricts dropping of individual silicon nitride grains during wear, and together with the higher fracture toughness and hardness are the reasons why the materials doped by Lu exhibited the highest wear resistance. The same wear mechanisms have been observed for all studied materials which consist of the combination of mechanical wear (micro-fracture) and tribochemical reaction. Except the fracture toughness, the Si₃N₄-SiC micro/nano composites exhibited the higher mechanical properties compared to those of Si₃N₄ monoliths.

Selected publications:

[1] P. Tatarko, M. Kašiarová, J. Dusza, J. Morgiel, P. Šajgalík, P. Hvizdoš, Wear resistance of hot-pressed Si₃N₄/SiC micro/nanocomposites sintered with rare-earth oxide additives. *Wear*, 2010, vol. 269, p. 867-874

[2] P. Tatarko, Š. Lojanová, Ján Dusza, P. Šajgalík, Influence of various rare-earth oxide additives on microstructure and mechanical properties of silicon nitride based nanocomposites. *Materials Science and Engineering A - Structural Materials Properties Microstructure and Processing*, 2010, vol. 527, p. 4771-4778

[3] Š. Lojanová, P. Tatarko, Z. Chlup, M. Hnatko, J. Dusza, Z. Lenčič, P. Šajgalík, Rare-earth element doped Si₃N₄/SiC micro/nano-composites-RT and HT mechanical properties. *Journal of the European Ceramic Society*, 2010, vol. 30, p. 1931-1944

[4] P. Tatarko, Š. Lojanová, J. Dusza, P. Šajgalík, Characterization of rare-earth doped Si₃N₄/SiC micro/nano-composites. *Processing and Application of Ceramics*, 2010, vol. 4, no. 1, p. 25-32

Applications

Title of the achievement: Preparation method of composite systems

It was developed a method of the preparation of high porous composite systems on polyhydroxybutyrate-chitosan and polyhydroxybutyrate-chitosan-calcium phosphate basis. The advantage of the method is elimination of toxic halogen organic solvents standardly applied in the preparation process of used polymer mixture. The method allows to obtain of bioactive composite with the high fraction (up to 80 wt%) of nanocrystalline calcium phosphate filler (e.g. nanohydroxyapatite), which significantly enhanced its bioactivity. The porous structure with pore size up to 100 μm improves composite properties in relation to the formation and ingrowing of new tissue after their implantation into body.

MEDVECKÝ, L.: Method of the preparation of composite systems. Pat. Appl. No. PP 00106-2010. Úrad priemyselného vlastníctva SR 2010

Title of the achievement: Anisotropy of deformation process and its use in deformation induced grain growth.

Technological and thermal conditions of unconventional cold rolling with low reduction were optimized using mathematical modeling. The optimization of the rolling conditions was investigated at temperatures of hindering of recovery processes in ferrite of isotropic electrotechnical steels. This was done in order to achieve maximal intensity of deformation hardening in center of the sheet thickness and minimum in surface/subsurface layer. After subsequent thermal exposition such deformation state of the material provides diffusion controlled columnar grain growth from the surface/subsurface layer towards the sheet thickness center.

Nano-indentation tests were used in analysis of deformation processes in a measure of particularly oriented grains of silicon ferrite. Using EBSD analysis the grains were selected according to their crystallographic orientation in three groups i.e.: deformation, Goss and cubic orientations. The deformation strain-stress curves in particular grain orientations were determined with use of spherical indenter. The values of deformation intensities were optimized on a base of different behavior of the strain-stress curves for different crystallographic orientations. This was done in such a way to provide deformation induced grain growth of grains with cubic or Goss crystallographic orientation at the expense of the grains with unwanted deformation orientation.

The information obtained on a base of these experiments allows us to optimize of technological parameters of rolling of isotropic electrotechnical steels. This was done in order to provide deformation gradients through sheet thickness and between grains with particular crystallographic orientations. The deformation gradients is used as driving force of grain boundary motion for columnar ferrite grains development with domination of cubic or Goss crystallographic orientation.

In frame of Structural Funds of EU program:

Technology of preparation of electrotechnical steels possessing high permeability for high affectivity electromotors. ITMS 26220220037. Call: Transfer to praxes the knowledge and technology obtained by research and development OPVaV-2008/2.2/01-SORO

Stoyka, V. Kováč, F. Stupakov, O. Petryshynets, I.: Texture evolution in Fe-3% Si steel treated under unconventional annealing conditions, *Materials Characterization*, 61, 2010, s.1066-1073

Gavendová P., Kováč F., Stoyka V., Petryshynets I., Kvačkaj T.: Effect of temper rolling on the strain hardening of non-oriented electrotechnical steel. *Acta Metallurgica Slovaca*, Vol. 16, 2010, No.3, p. 181-186

Petryshynets I., Stoyka V., Zubko P., Gavendová P., Kováč F.: Dependence of grains hardness on crystallographic orientation in electrotechnical steels, *Acta Metallurgica Slovaca Conference*, 2010, no. 1, p.238-241

Title of the achievement: Fatigue properties of low carbon of advanced ultrahigh strength steels

VEGA project "Fatigue properties of low carbon of advanced ultrahigh strength steels"
No. 2/0195/09, (2009-2011)

One of the main goal of the project is development of a new low carbon steel that have tensile strength of at least about 700 MPa with the trade-off balance between strength-ductility and fatigue properties designated primarily for applications of automotive industry. The research is oriented on the investigation the influence of the chemical composition and various parameters of the thermo-mechanical and/or heat treatments processing. Ten studied steels, basically low carbon and low alloy steels with or without microalloying elements, were melted in laboratories of Research and Development Center of US Steel Košice. The systematic investigations of different modes of controlled rolling and cooling as well as the influence of intercritical annealing conditions for both hot and cold rolled steels, on the microstructure changes and on the tensile properties steels were realized. The experimental results show that by an unconventional thermomechanical control processes in combination with a cold rolling and the optimal heat treatment is possible to obtain ultrafine-grained DP steels which has excellent mechanical properties.

Our research is oriented also on the investigation of possibilities for improvements of the fatigue resistance of steels, including utilization of the surface engineering technologies. Experiments were carried out on sheets of dual phase steel and it was showed, that shot peening can be considered as an alternative technology to fatigue life improvement of HDT580X steel on level of ultra high strength steels ($R_m > 700$ MPa).

International Scientific Projects

Title of the achievement: MNT - ERA.NET **Hard Nanocomposite Coatings** – HANCOC

The optimization of PECVD deposition process of WC-C coatings using carbonyl method within MNT - ERA.NET **Hard Nanocomposite Coatings** (HANCOC) project resulted in the nanocrystalline structure, hardness increase up to 40-60% up to ~ 28 GPa and coefficient of friction of ~0.1. Simultaneously, elastic mapping of the coating with the stiffness exceeding 200 GPa at nanoscale was achieved using the newest AFM method.

Selected publications:

1. LOFAJ, František - NĚMEČEK, Jiří - BLÁHOVÁ, Olga. A comparative study of nanoindentation measurements on thin coatings. Chemické listy, 2010, roč. 104, s. 271-274. (0.717 - IF2009). (2010 - Current Contents). ISSN 0009-2770
2. LOFAJ, František - HVIŠŤOVÁ, Petra - DUSZOVÁ, Annamária: Wear mechanism of WC-C coatings. In Metalurgija, 2010, vol. 49, no. 3, p. 215. (0.439 - IF2009). ISSN 0543-5846
3. KOTTFER, Daniel – FERDINANDY, Milan: Tenké vrstvy, FjF TUKE Edícia študijnej literatúry, Košice, 2010, 100 s. ISBN 978-80-553-0359-8. Podiel domácich autorov: 45%
4. KRÁL, Jozef - FERDINANDY, Milan - KOTTFER, Daniel - MAŇKOVÁ, Ildikó - CENIGA, Ladislav: Tribological and refractory properties of TiAl3 intermetallic alloy. In Surface Review and Letters, 2009, vol. 16, no. 4, p. 623-629. (2009 - Current Contents). ISSN 0218-625X

Submitted patents:

1. FERDINANDY, Milan - DUSZA, Ján - LOFAJ, František: Spôsob prípravy vrstiev W, Cr, Mo, ich karbidov, nitridov, silicidov, multivrstvových a kompozitných štruktúr na pevných substrátoch a zariadenie pre ich prípravu : patentová prihláška vynálezu : Úrad Priemyselného vlastníctva SR, číslo prihlášky: PP29-2008
2. KOTTFER, Daniel - FERDINANDY, Milan - DUSZA, Ján - LOFAJ, František: Spôsob a zariadenie pre povrchovú úpravu vnútorných plôch rotačných telies : patentová prihláška vynálezu : Úrad Priemyselného vlastníctva SR, číslo prihlášky: PP85-2008. Podiel domácich autorov: 60%
3. FERDINANDY, Milan - DUSZA, Ján - LOFAJ, František - KOTTFER, Daniel: Zariadenie pre prípravu vrstiev karbidov, nitridov, silicidov, boridov W, Cr, Mo, Re, Os, Rh, Ru a multivrstvových a kompozitných štruktúr na vnútornej valcovej ploche elektricky vodivej rúry. Prihláška patentu - reg. číslo PP95 – 2009. Podiel domácich autorov: 80%
4. KOTTFER, Daniel - FERDINANDY, Milan - DUSZA, Ján - LOFAJ, František: Zariadenie pre vytváranie ochranných vrstiev na vnútorných plochách rotačných telies odparovaním látky elektrónovým lúčom. Prihláška patentu - reg. číslo PP151 – 2010. Podiel domácich autorov: 50%