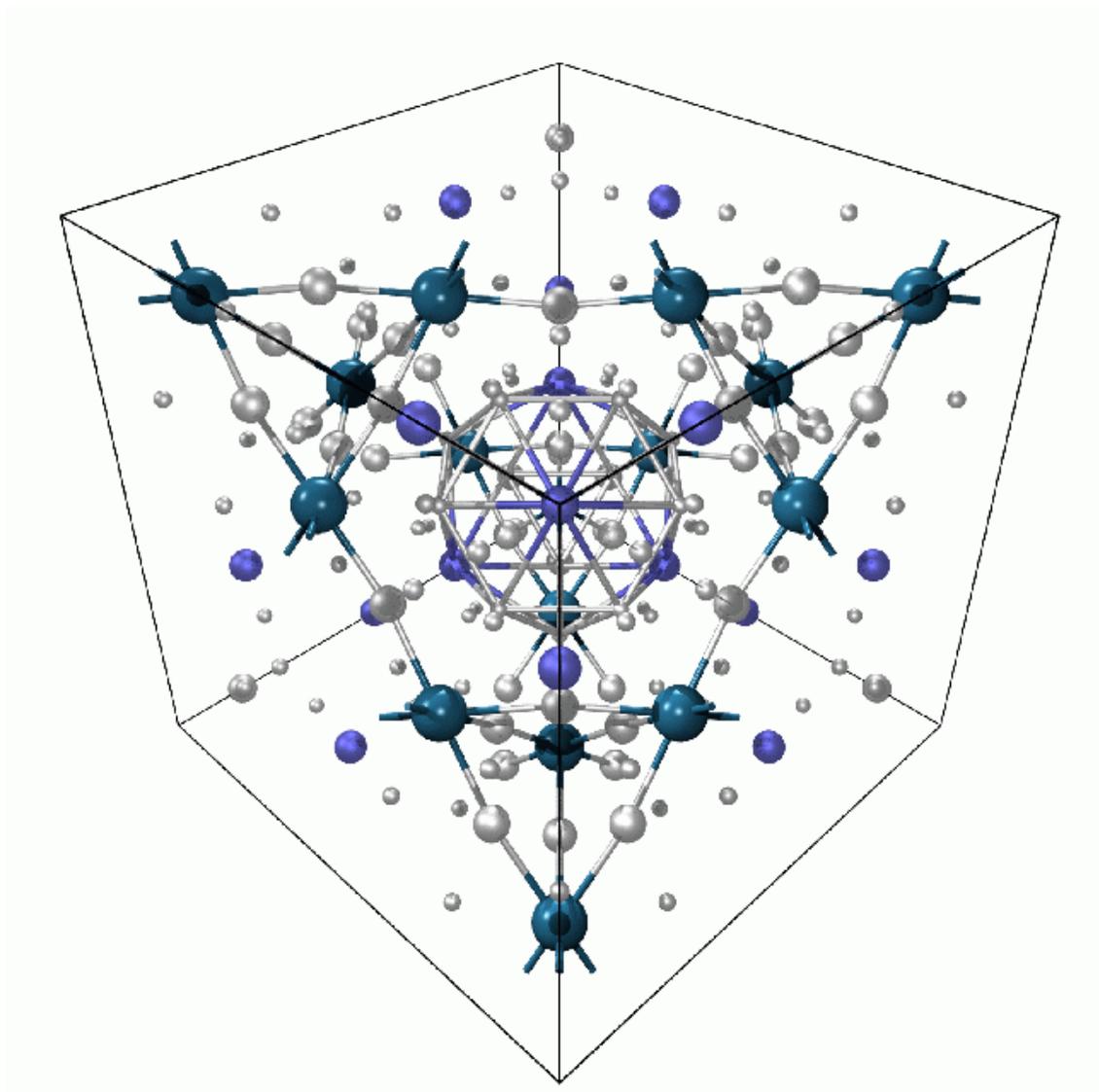


# NANOVED 2013 & NANO INFO DAY

6th International Conference  
on Nanosciences, Nanotechnologies, Nanomaterials  
and NANO INFO DAY of the Nanoforce Project



## Program and Abstracts

*Svit, Slovakia, September 22 – 25, 2013*



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# **NANOVED & NANO INFO DAY 2013**

6<sup>th</sup> International Conference on Nanosciences, Nanotechnologies, Nanomaterials  
and NANO INFO DAY of the Nanoforce Project

Program and Abstracts

Editors:

Peter Švec  
Ivo Vávra  
Silvia Surová

Slovak Academy of Sciences  
and Association of Chemical and Pharmaceutical Industry of the Slovak Republic

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**NANOVED & NANO INFO DAY 2013**  
**6<sup>th</sup> International Conference**  
**on Nanosciences, Nanotechnologies, Nanomaterials**  
**and NANO INFO DAY of the Nanoforce Project**

**Svit, Slovakia, September 22 - 25, 2013**

**Organizers**

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Institute of Experimental Physics, Slovak Academy of Sciences  
Institute of Physics, Slovak Academy of Sciences

Association of Chemical and Pharmaceutical Industry of the Slovak Republic

Nanoforce Project

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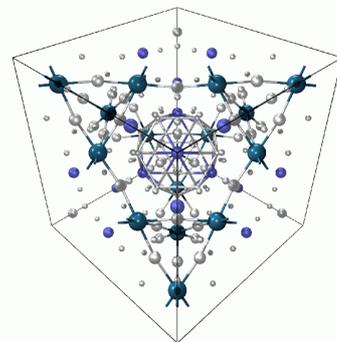
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# NANOVED 2013 & NANO INFO DAY



## 6<sup>th</sup> International Conference on Nanosciences, Nanotechnologies and Nanomaterials joined with Nano Info Day Svit, Slovakia, September 22 – 25, 2013

Hotel Spolcentrum Svit, Slovakia

### Programme

**Sunday, September 22, 2013**

16:00 - 20:00 Registration

19:00 - 21:00 Welcome and refreshments

**Monday, September 23, 2013**

08:00 - 09:00 Registration (continued)

#### Opening ceremony

Chairperson: **M. Budzák**, General Director of VUCHV Svit

09:00 - 09:10 **M. Budzák**: Welcome to the participants

09:10 - 10:00 **Inaugural addresses**

**Roman Karlubík**, president of the Association of Chemical and Pharmaceutical Industry of the Slovak Republic

**Michal Lach**, Director of the Board, Chemosvit Folie a. s.

**Jaromír Pastorek**, president of Slovak Academy of Sciences

**Robert Redhammer**, rector of the Slovak Technical University

**Lýdia Šuchová**, director of APVV

**10:00 - 10:30 Coffee Break**  
**Joint Session 1: Nano Info Day & Nanoved**

**Chairperson: Peter Švec**

- 10:30 - 11:15**    **A. Gedanken:** AntiBacterial, AntiViral, Anti biofilms and Antifungal Nanoparticles and their Sonochemical Coatings on Surfaces (Textiles and Glas) (invited lecture)
- 11:15 - 12:00**    **F. Šimančík:** Nanostructuring - powerfull tool for tailoring of aluminium properties (invited lecture)

**12:30 - 14:00 Lunch Break**

**Joint Session 2: Nano Info Day & Nanoved**  
*Nanomedicine and Health Risks*

**Chairperson: S. Surová, Secretary General, the Association of Chemical and Pharmaceutical Industry of the Slovak Republic**

- 14:00 - 14:20**    **S. Surová:** NANOFORCE Project
- 14:20 - 14:50**    **J. Kukutschová:** Ultrafine, fine and coarse particles in automotive wear debris and their environmental impact (invited lecture)
- 14:50 - 15:10**    **A. Gábelová:** The biological activity of magnetite nanoparticles
- 15:10 - 15:30**    **J. Tulinská:** : Interactions of nanoparticles with the immune system – possibilities of safety assessment
- 15:30 - 15:50**    **M. Drličková:** Nanomaterials in REACH (in Slovak)

**15:50 - 16:20 Coffee Break**

**Joint Session 3: Nano Info Day & Nanoved**  
*Nanoparticles - Preparation Methods*

**Chairperson: Ivo Vávra**

- 16:20 - 16:50**    **N. Tarasenko:** Laser and plasma assisted fabrication and modification of nanoparticles in liquid: (invited lecture)
- 16.50 - 17.10**    **P. Lobotka:** Preparation of nanoparticles by vacuum deposition on the Ionic liquid surface
- 17:10 - 17:30**    **M. Antalík:** Progress in chemical methods of nanomaterials preparation
- 17:30 - 17:50**    **G. Kratošova:** Biological production of metallic nanoparticles (invited lecture)

**18:00 - 19:30 Poster Session**

**19:30 - 21:00 Dinner**

**Tuesday, September 24, 2013**

**Session 4: Magnetic Nanomaterials – Processing and Properties**

**Chairperson: M. Deanko**

**09:00 - 09:30 R. Varga:** Nanocrystalline microwires for sensoric applications (invited lecture)

**09:30 - 10:00 I. Škorvánek:** Magnetic processing of amorphous and nanocrystalline alloys (invited lecture)

**10:00 - 10:40 J. Pištora:** Fundamental aspects of magneto-optics (invited lecture)

**10:40 - 11:00 Z. Gažová:** Nanomaterials and amyloid aggregation of proteins

**11:00 - 11:30 Coffee Break**

**Session 5: Surfaces and Catalysis**

**Chairperson: J. Kukutschova**

**11:30 - 12:10 M. Hronec:** Nanomaterials in catalysis (invited lecture)

**12:10 - 12:50 M. Krajci:** Catalytical properties of complex intermetallic surfaces (invited lecture)

**13:00 - 14:00 Lunch Break**

**Session 6: Ceramic Nanocomposites**

**Chairperson: M. Hronec**

**14:00 - 14:30 J. Dusza:** Silicon nitride + graphene platelet nanocomposites (invited lecture)

**14:30 - 14:50 F. Lofaj:** Nanocrystalline superhard coatings

**14:50 - 15:10 M. Kašiarová:** Development and characterisation of Si<sub>3</sub>N<sub>4</sub>-SiC ceramic nanocomposites for high temperature applications

**15:10 - 15:40 Z. Lenčes:** Processing and properties of SiC-CNT and Al<sub>2</sub>O<sub>3</sub>-CNT nanocomposites (invited lecture)

**15:40 - 16:00 P. Tatarko:** Development and mechanical properties of ZrO<sub>2</sub> ceramic nanocomposites reinforced by boron nitride nanotubes

**16:00 - 16:30 Coffee Break**

**Session 7: Nano - materials production in RIMMF & Chemosvit, ltd. excursion**

**Chairperson: Michal Eách, Martin Budzák**

**16:30 - 19:00** Excursion and company presentation

**19:30 - 22:30 Conference Banquet**

**20:00 Best Young Researcher Contribution Award Ceremony**

**Wednesday, September 25, 2013**

**Session 8: Nanocomposites and Nanoparticles**

**Chairperson: T. Kvačkaj**

**09:00 - 09:30**    **K. Iždinský:** Metal matrix composite materials - structure and interfaces (invited lecture)

**09:30 - 10:00**    **A. Michalcová:** Preparation of metallic nanoparticles by selective leaching (invited lecture)

**10:00 - 10:30**    **M. Jergel:** Formation of nanoparticle arrays by self-assembly (invited lecture)

**10:30 - 11:00**    **Coffee Break**

**Session 9: Nanocomposites – Structure Characterization**

**Chairperson: J. Pištora**

**11:00 - 11:20**    **T. Kvačkaj:** Asymmetric Rolling as SPD Technology

**11:20 – 11:40**    **T. Hatala, M. Miglierini** - Crystallization processes in NANOPERM-type nanocrystalline alloys studied by CEMS, CXMS, and NIS techniques

**11:40 - 12:00**    **P. Švec:** Precession electron diffraction of fine-grained structures

**12:00 - 12:20**    **I. Vávra:** TEM characterization of nanoparticles and their penetration into human cells

**12:20 - 12:30**    **Closing remarks**

**12:30 - 14:00**    **Lunch**

**End of the Conference**

## List of Poster Contributions

- P01: B. Buliaková, M. Mesárošová, M Šelc, A. Gábelová,**  
The effect of magnetite nanoparticles on cell signaling in the human tumor lung cells
- P02: V. Holišová, M. Natštinová,**  
Reaction of Soman (GD) with suspensions containing gold and silver nanoparticles
- P03: P. Kunzo, P. Lobotka, E. Kovacova, V. Smatko, I. Vavra,**  
Nanocomposites of polyaniline and inorganic nanoparticles prepared in ionic liquids.
- P04: R. Bidulský, J. Bidulská, M. Actis Grande, M. Maccarini,**  
Compaction of soft magnetic materials with aluminium addition
- P05: J. Bidulská, R. Bidulský, R. Kočiško, T. Kvačkaj,**  
Possibilities of ECAP and ECAR in powder metallurgy area
- P06: E. Kováčová, V. Šmatko, P. Kunzo,**  
Vacuum deposition of metals onto liquid substrates
- P07: V. Šmatko, P. Hvizdoš, I. Vávra,**  
Cross-sectional structural analysis of the nano-indent region in molybdenum nanoporous thin film
- P08: N. N. Tarasenko, A. V. Butsen, I. Vavra, P. Lobotka, N. V. Tarasenko,**  
Properties of metal nanoparticles prepared by pulsed laser ablation in ionic liquid
- P09: M. Kubovčíková, M. Koneracká, V. Závíšová, M. Múčková, N. Tomašovičová, M. Timko, E. Schmidtová, P. Bartoš, P. Kopčanský,**  
Biodistribution of Paclitaxel in the form of magnetic nanospheres
- P10: P. Švec, P. Švec Sr., D. Janičkovič,**  
Monophase Fe<sub>23</sub>B<sub>6</sub>-type alloy formed by crystallization of rapidly quenched Fe-Ni-Nb-B system
- P11: I. Mat'ko, E. Illeková, P. Švec Sr., P. Švec, D. Janičkovič, V. Vodárek,**  
Nanocrystalline phase elaborated by thermally activated crystallization of amorphous Fe-Sn-B ribbons.
- P12: I. Janotova, P. Svec Sr., I. Matko, D. Janickovic, P. Svec,**  
Structure and Kinetics of Metastable Systems based on Fe-Co-B-Si-(P)-(Cu)
- P13: D. Janickovic, J. Zigo, P. Švec, I. Mat'ko, P. Švec Sr.,**  
On the structure evolution in q-phase rapidly solidified Al<sub>65</sub>Fe<sub>15</sub>Si<sub>20</sub> composite





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# NANOFORCE

Zväz chemického a farmaceutického priemyslu Slovenskej republiky

Silvia Surova

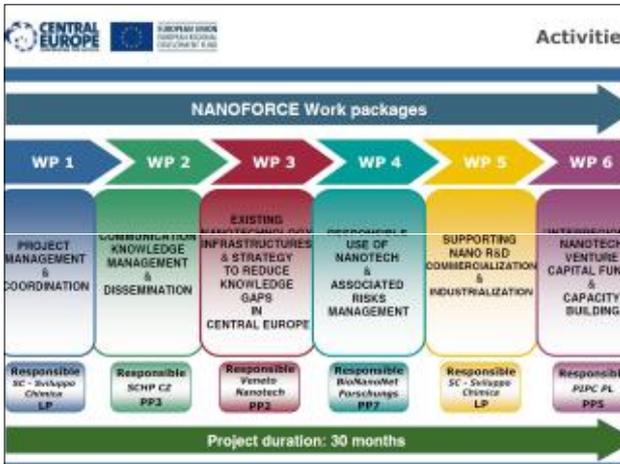
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**Researchers, Venture Capitalists & Managers**

The integration of scientific competences, venture capital and management is the key factor of success for the nanotechnologies, wherever in the world! At NANOFORCE we offer the chance to propose your deal! We mean ... not only an idea please ... but something more formalized... data, patents, pilot plant ... incorporation or expansion of your company. You have several routes to enter in contact with your Partners:

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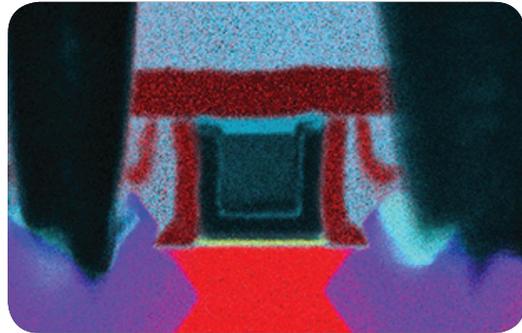
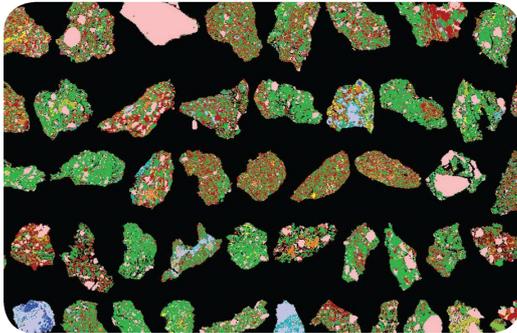
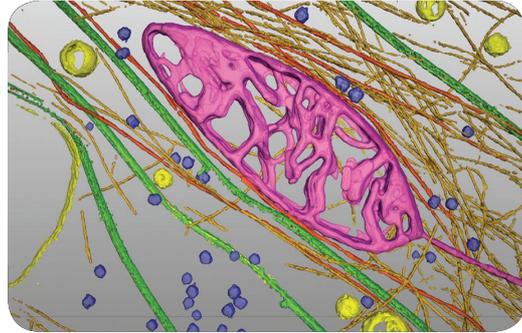
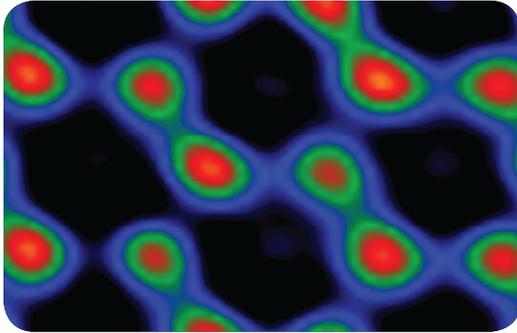
**Doterajšie výsledky:**

- Zmapovanie používania a prípravy nanočastic v zúčastnených krajinách - správa
- Zmapovanie legislatívneho stavu ohľadom nanočastic v EU a jednotlivých partnerských krajinách - správa
- Organizácia Nano Info dní v jednotlivých krajinách - v septembri 2012 vo Svite
- Organizácia Okrúhlych stolov - diskusia s národnými autoritami a priemyslom 22.1.2013 v Bratislave
- Príprava a preklad webstránky [www.nanoforceproject.eu](http://www.nanoforceproject.eu), informačných listov a brožúry Nanoforce
- Organizácia Workshupu Nanodeal Generator 28.2.2013, prezentácie na webe
- Účast mladých výskumníkov na školení Nanoforce v Prahe v júni 2013
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- Nano Info Say spolu s konferenciou Nanovend – vo Svite dňa 22.-25. septembra 2013
- Brožúra Nanoforce – 10 operačných postupov
- Príprava 2. okrúhleho stola so zástupcami dotknutých ministerstiev
- Uploading 8 dealov na web [www.nanoforceproject.eu](http://www.nanoforceproject.eu)
- Prezentácia vybraných dealov na [NanotechItaly2013 Call for Start-Up](#) v novembri 2013

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**(Top left)** Atomic resolution phase image of graphene. Sample courtesy of N. Alem and A. Zettl, University of California, Berkeley. Images Joerg Jinschek and Emrah Yucelen, FEI, Hector Calderon, IPN, Mexico, and C. Kisielowski, NCEM, USA. Exit wave reconstruction by Joerg Jinschek. **(Top right)** Surface rendered cryo electron tomogram of mouse fibroblast cell. Courtesy of Roman Koning. **(Bottom left)** Drill cuttings from a CO<sub>2</sub> injection well. Courtesy CO2CRC, Australia. **(Bottom right)** 600 × 600 pixel maps, fully quantified, of a 45 nm PMOS transistor structure. Courtesy of D. Klenov, FEI NanoPort, The Netherlands • Tecnai Osiris™ S/TEM.

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## **Abstracts**

### **Invited Lectures and Oral Contributions**



# Coating Anti Bacterial, Anti Viral, Antibiofilm and Antifungi Nanoparticles on Flat and Curved Surfaces Employing the Sonochemical Method

Aharon Gedanken

*Department of Chemistry, Bar-Ilan University, Ramat-Gan, 52900, Israel*

Sonochemistry is an excellent technique to coat functional nanomaterials on various substrates, and imparting new properties to the substrates.

After a short demonstration of coating NPs on ceramics and stainless steel, I'll present the coating of textiles such as polyester, cotton, nylon, and nonwoven. In all cases a homogeneous coating of NPs was achieved. Silver is known for generations as antibacterial, and indeed the Ag NPs have killed the gram-negative *E. Coli* (strain 1313) as well as the gram-positive *Staphylococcus aureus* (strain 195) bacteria very efficiently<sup>1</sup>. Lately, since the FDA shows less enthusiasm towards nanoAg we have moved to NPs of ZnO, CuO and MgO as antibacterial agents. They were coated on the above-mentioned fabrics and showed excellent antibacterial properties<sup>2</sup>. The coated textiles were examined for the changes in the mechanical strength of the fabric. A special attention was dedicated to the question whether the NPs are leaching off the fabric when washed repeatedly. The coated ZnO NPs on cotton underwent 65 washing cycles at 92 °C in water in a Hospital washing machine, no NPs were found in the washing solution and the antibacterial behavior was maintained. Our vision is that all the textiles in the Hospitals of the future will be coated by antibacterial NPs<sup>3</sup>. The mechanism of killing the bacteria was studied and will be presented. Our research in the last few months was directed towards finding nanomaterials that can kill resistant bacteria. I will present recent results on NPs of antibiotic materials, as well as inorganic NPs that can do this job.

MgF<sub>2</sub> NPs coated on glass have demonstrated Antibiofilm Activity. The ability of bacteria to colonize abiotic surfaces and develop biofilms is a major cause of medical implant-associated infections and results in prolonged hospitalization periods and patient mortality. Here, we report on the synthesis of nanosized fluorides materials (MgF<sub>2</sub> NPs) and we prove the affecting interactions with bacterial cells by mechanical, potential damages to the membrane and the possibility to interact with nucleic acids. We have extended these first attempts and coated Latex catheters by these MgF<sub>2</sub> NPs. The coated catheters showed resistance to the development of biofilms on their surface.

The antiviral activity of Ag- or Au-MES (mercaptoethanesulfonate) against HSV-1 and 5 different influenza viruses will be demonstrated. The ideology behind the design of this antiviral agent was that these viruses attack first the heparin sulfate in the cell. It is therefore proposed that a NP having many sulfate ions as the end group will "cheat" the virus to attack the NP instead of the human cell.

## References

- [1] Perelshtein, I. , Applerot, G. , Perkas, N. , Guibert, G. , Mikhailov, S. , Gedanken, A. *Nanotechnology*, 19, Article Number: 245705 (2008).
- [2] Perelshtein, I. , Applerot, G. , Perkas, N. , Wehrschetz-Sigl, E. , Hasmann, A. , Guebitz, G. M. , Gedanken, A. *ACS Appl. Mater. & Interf.* , 1, 363-366 (2009).
- [3] Ilana Perelshtein, Yelena Ruderman; Nina Perkas, Jamie Beddow, Gagandeep Singh, Mircea Vinatoru, Eadaoin Joyce, Timothy J Mason, , María Blanes, Korina Mollá, Aharon Gedanken, *Cellulose* 20, 1215-1221 (2013).

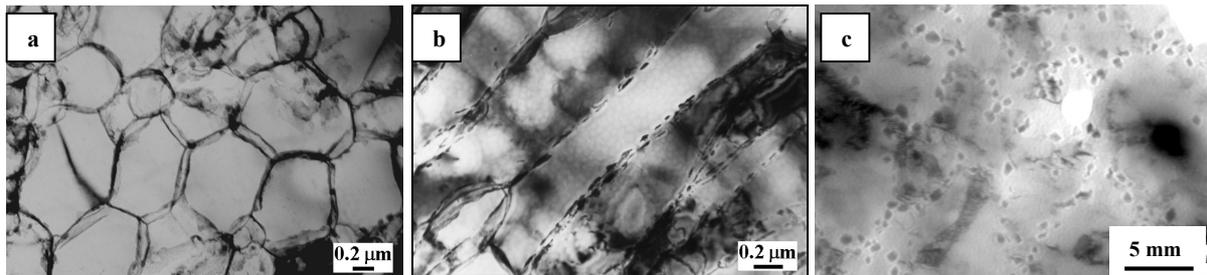
# Nanostructuring - powerful tool for tailoring of Aluminium properties

František Šimančík, Martin Balog

*Institute of Materials and Machine Mechanics SAS, Bratislava, Slovakia*

There are many possibilities how to improve important mechanical properties of structural materials, such as strength, stiffness, fracture toughness, creep resistance, etc. Most of these approaches are based on alloying followed by proper thermal treatment or by making composites. Nevertheless, it appears that proper tailoring of microstructure itself can be regarded as a very powerful tool for this purpose as well.

The effect of different technological methods providing variable microstructures of the identical material on its mechanical properties will be particularly demonstrated on aluminium powder compacts. Their microstructure usually includes a small portion of aluminium oxides coming from the surfaces of initial powders. Depending on processing route, the amorphous ~4 nm thick native  $\text{Al}_2\text{O}_3$  layer either disrupts into separate nano-metric dispersions or remains as continuous 3D skeleton within final compact and substantially contributes to structure stabilization at elevated temperatures. The distribution and morphology of oxides and grain size (Fig.1) exhibit a decisive influence almost on all mechanical properties. Remarkable improvement of the material performance in many applications can be thus achieved by proper tailoring of some microstructural features. Successful application cases including engine pistons of racing cars with excellent structural stability, stiffness and creep resistance will be presented.



**Fig. 1:** Bright field TEM micrographs of Al compacts prepared by forging (a), ECAP (b) and hot isostatic pressing (c) of identical Al powders revealing different compaction morphologies.

## Acknowledgment

This article has been produced with the financial assistance of the European Regional Development Fund (ERDF) for projects: ITMS 26240220073 “Competence centre for new materials, advanced technologies and energy” and ITMS 26220220154 “Competence center for industrial research and development in the field of light metals and composites”.

# Nanoforce Project

Silvia Surova

*Association of the Chemical and Pharmaceutical Industry of the Slovak Republic,  
Bratislava, Slovakia*

## General project objective

In line with the EU Strategy for Nanotechnology (2004) and the EU Action Plan for Nanoscience & Nanotechnology (2009), the general objective of NANOFORCE project is to foster the innovative nanotechnology-sector networks across Central Europe regions by bringing together public and private organizations (enterprises, research centers, venture capitalists and public institutions) to carry out collaborative & interdisciplinary researches on nanomaterials (in the frame of REACH Regulation) and to turn the most promising laboratory results into innovative industrial applications, not only to produce new materials but also to improve the industrial sustainability (more security & lower environmental impact in the life cycle of products).

## Specific project objectives

According to the strategy of expanding industrial-oriented researches in the nanotechnology sector within the concerned Central Europe regions, the specific objective of NANOFORCE project are:

- 1) Recommendations for the European Commission to advance potential changes of REACH regulation for some specific nanomaterials according to the risk assessment carried out on the selected nanomaterials
- 2) The identification of 100 potential deals between R&D Centre and large SM Enterprises of Central Europe involved regions to turn researches into industrial processes
- 3) Nanotechnology roadmap for CE space composed by the Technological Rating and Business Plan
- 4) To design the Venture Capital Fund of by Transnational investors.

## Project website

Register your project or deal proposal as a researcher: [www.nanoforceproject.eu](http://www.nanoforceproject.eu)

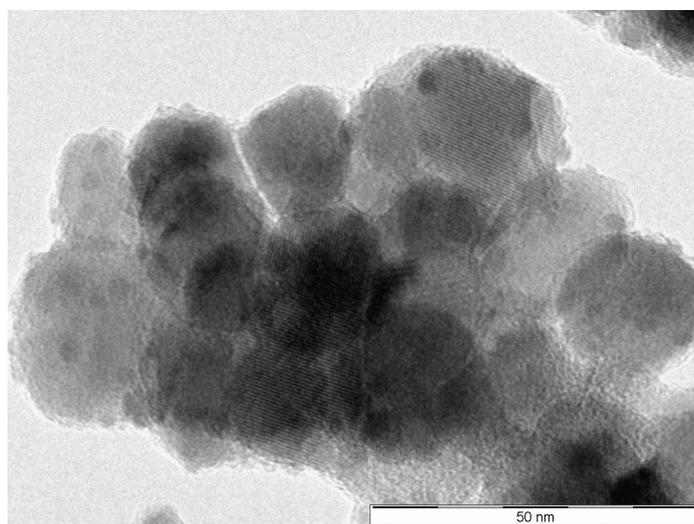
## Ultrafine, fine and coarse particles in automotive wear debris

<sup>1\*</sup>Jana Kukutschová, <sup>1</sup>Vlastimil Matějka, <sup>1</sup>Pavλίna Peikertová, <sup>1</sup>Miroslav Vaculík,  
<sup>1,2</sup>Peter Filip

<sup>1</sup>*Nanotechnology Centre, VŠB-TU Ostrava, 17. listopadu, 70833 Ostrava-Poruba, Czech Republic*

<sup>2</sup>*Center for Advanced Friction Studies at SIU Carbondale, Mailcode 4343, Carbondale, IL 62901, USA*

More than a billion registered vehicles worldwide generate considerable amounts of gaseous and particulate pollutants. While the emissions related to exhaust gasses and tire wear were addressed extensively, the released brake wear debris and its impact were studied to a considerably lesser extent. Our previous work indicated that the released wear debris can have negative impact on environment. A characteristic automotive brake pad is a multicomponent composite typically formulated of more than 10 constituents. Manufacturers of brake pads worldwide use several thousand different raw materials, e.g. various metals and their compounds, carbon-based components and many others. The contribution addresses the character of wear debris released from a model “low metallic” and commercial friction materials, used in a typical brake in Europe, USA and Asia. Brake samples were subjected to the standardized brake dynamometer test simulations (Link Engineering) and collected wear particles were further studied using a High Resolution Transmission Electron Microscopy (HRTEM – Hitachi 7100) equipped with the Energy Dispersive X-ray Microanalysis (EDX – Noran Voyager), and used in a series of genotoxicity bioassays (Ames test and SOS Chromotest). Our experiments demonstrated that airborne wear particles with sizes between 10 nm and 20  $\mu\text{m}$  can be released into the air (see the Figure). Elemental and phase analysis revealed the presence of numerous compounds which were not present in the original brake material. Nano-sized Cu, Fe, and Sn oxides and carbon particles were confirmed in the released coarse, fine and ultrafine wear debris fractions. The genotoxicity tests demonstrated mutagenic potency of wear particles in all bioassays used. These findings proved contribution of non-combustion processes associated with braking of automobiles to nano-particulate air pollution which may potentially pose health risks in areas with heavy traffic.



TEM image of ultrafine particles emitted from a model friction composite

## The biological activity of magnetite nanoparticles

<sup>1\*</sup>Gábelová, A., Mesárošová, M., <sup>2</sup>Závišová, M., <sup>2</sup>Koneracká, M., <sup>3</sup>Ursínyová, M., <sup>1</sup>Chalupa, I.,  
<sup>1</sup>Kozics, K., <sup>1</sup>Buliaková, B., <sup>2</sup>Tomašovičová, N., <sup>4</sup>Labudová, M., <sup>5</sup>Vávra, I., <sup>5</sup>Križanová, Z.,  
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Magnetite is one of the most used forms of iron oxide nanoparticles. Magnetite nanoparticles (MNPs) are being utilized for a plethora of biotechnological and biomedical applications, e.g. as contrast agents in magnetic resonance imaging (MRI), for enzyme immobilization, targeted cell/macromolecules separation and purification, cell labeling and sorting, magnetofection, as heating mediators in hyperthermia or as nanocarriers in targeted drug/gene delivery. Although the benefit of MNPs is obvious, a thorough investigation of the nanoparticle biosafety and understanding of the nanoparticle-cell interactions is an urgent need.

This study deals with the biological activity of magnetic nanoparticles with magnetite core of size 7.6 nm and different hydrophilic shells in human lung adenocarcinoma epithelial cell line A549 and human embryo pulmonary fibroblasts HEL 12469. MNPs were synthesized by a chemical co-precipitation of ferric and ferrous salts in alkali aqueous medium, coated with various synthetic moieties and characterized in depth by different physicochemical methods. The particle uptake, distribution and accumulation in the cells were observed by transmission electron microscopy (TEM) and the internalized amount of MNPs was quantified by atomic absorption spectrometry (AAS). The cell viability, genome integrity (DNA breakage, micronucleus formation and chromosomal aberrations), oxidative status (the oxidative damage to DNA, the levels of intracellular reactive oxygen species, ROS, and the activity of antioxidant enzymes), changes in cell signaling and cytoskeletal structure were assessed under control and MNPs exposed conditions. Our study provides a comprehensive investigation of the impact of MNPs on human cells *in vitro*. Moreover, some of the challenges for future studies are discussed.

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## Interactions of nanoparticles with the immune system – possibilities of safety assessment

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The interaction between nanoparticles (NPs) and immunocompetent cells has been published; however, the data available are limited. Assessment of the immunotoxicity of nanomaterials is essential for safe use of pharmaceutical and consumer nanoproducts. Toxicological data of the bulk material cannot be simply transferred to NPs and therefore development of appropriate *in vitro* tests and cellular models is required. It is known that size, surface charge, hydrophilicity, lipophilicity, catalytic activity and the steric effects of particle coating can affect NP compatibility with the immune system.

Nanoparticles can be engineered to either avoid immune system recognition or specifically inhibit or enhance the immune responses. However, because NPs are often first picked up by the phagocytic cells of the immune system (*e.g.* macrophages), there may be undesirable interactions between nanoparticles and the immune system, such as immunostimulation or immunosuppression. Stimulation may promote inflammatory or autoimmune disorders. On the one hand, immunosuppression may increase the host's susceptibility to infections and cancer.

Human peripheral blood is a very useful biological material for *in vitro* screening of the immunotoxic potential of chemicals including nanoproducts. Blood is a model for the first target in the case of intravenous administration of NPs used in medical diagnostics and therapy and a surrogate target model for other routes of exposure, giving information on the overall body response to environmental and industrial pollutants.

A properly selected battery of *in vitro* immune assays might identify significant cells/molecules probably targeted by NPs. Immune function assays are reliable tests to monitor the action of immunocompetent cells. They are widely used to determine congenital or acquired immune disorders in clinical diagnostics. The function of lymphocytes can be monitored by the lymphocyte transformation test using liquid scintillation. The function of phagocytes can easily be determined by measurement of the phagocytic activity of granulocytes and monocytes using fluorescein-labelled *Staphylococcus aureus* with flow cytometry. Moreover, the respiratory burst of phagocytes using hydroxyethidine can be measured. Cytokine release can be monitored using ELISA or PCR. Also cytotoxicity of natural killer cells (flow cytometry) is a reliable method for monitoring of tumour defence and several papers have recommended this assay for assessment of immunotoxic potential.

### Acknowledgement

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## Nanomaterials in REACH

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Nanotechnology is rapidly expanding and is being used in various areas, such as health care, consumer products, electronics, energy technologies, food, and agriculture. Products underpinned by nanotechnology are forecast to grow from a global volume of 200 bn € in 2009 to 2 trn € by 2015. Although nanomaterials have the potential to improve the quality of life and contribute to industrial competitiveness in Europe, the rapid increase in their use raises questions regarding their potential effects on health and environment. There is a need to adequately assess and manage the potential risks of these new forms of materials, and even if manufacturers, importers and downstream users have to ensure the safe use of each substance (whatever its form) under REACH Regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals). This introduces new challenges for regulators (Commission and ECHA) as well as all other stakeholders.

In the light of current knowledge and opinions of the EU Scientific and Advisory Committees and independent risk assessors, nanomaterials are similar to normal chemicals/substances in that some may be toxic and some may not. Possible risks are related to specific nanomaterials and specific uses. Therefore, nanomaterials require a risk assessment, which should be performed on a case-by-case basis, using relevant information.

On the basis of the *Communication of second Regulatory review on Nanomaterials* (2012), the Commission concludes that REACH sets the best possible framework for the risk management of nanomaterials when they occur as substances or mixtures. Nanomaterials are covered by the definition of a „substance“ in REACH, even though there is no explicit reference to nanomaterials. However, many registration dossiers are unclear in whether and how they cover nanoforms of substances. The Risk assessment methods are applicable but more specific requirements for nanomaterials in REACH have proven necessary. Therefore, the Commission plans to modify some of the REACH Annexes based on the results of the NanoSUPPORT project and Impact assessment of possible changes of REACH Annexes. The proposal is being prepared in co-operation with the CARACAL subgroup (Competent Authorities for REACH and CLP) on nanomaterials ("CASG Nano") and should be submitted by the end of this year.

The presentation provides an overview of the implementation process of nanomaterials in REACH Regulation.

# Laser and plasma assisted fabrication and modification of nanoparticles in liquid

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Preparation of nano-sized particles with the well-defined morphology, structure and chemical composition are crucial for achieving their unique properties attractive for a variety of practical applications, including microelectronics, medicine, biophotonics. gas sensor technology, heterogeneous catalysis, etc. In this report plasma assisted methods based on a pulsed laser ablation (LA) and electrical discharge (ED) in liquid media are discussed. Both the developed techniques offer advantages eliminating the need in large-scale vacuum system (the laser ablation and discharges are performed at normal atmosphere), provide a good control over the synthesis process and allow the fast and flexible production of metallic and composite nanoparticles with desired parameters. In the frame of these techniques one can combine particle synthesis with functionalization, encapsulation and stabilization of products. Some other characteristics of the techniques: (i) high versatility and possibility of the synthesis of nanostructures with different stoichiometry as a function of solution nature and a target (electrode) material composition; (ii) narrow and controllable particle size distribution and (iii) possibility to scale-up the process.

Promising capabilities of the developed techniques for synthesis of metallic (Au, Ag, Cu, Gd, Co, Ni), bimetallic (Ag-Cu, Ag-Au) as well as oxide (ZnO, CuO, Gd<sub>2</sub>O<sub>3</sub>:Tb<sup>3+</sup>), carbide (WC, TiC) and silicide (GdSi) nanoparticles with some examples of application of synthesized materials were demonstrated in [1, 2].

In this review the results of our studies in the following fields will be presented and discussed:

- Preparation of functionalized magnetic nanoparticles on a base of nanoscale compounds and alloys of gadolinium for biomedical applications, for instance as agents in hyperthermia.
- Fabrication of semiconductor CuInSe<sub>2</sub> (CIS) nanocrystals suitable for incorporating into functional photovoltaic devices as well as doped ZnO nanoparticles for applications in blue/UV light emitting diodes.
- Laser induced modification of synthesized nanoparticles. Development of optical diagnostics for in situ monitoring of the formation of intermediates and final nanosized particles in solutions.
- Development of novel plasma laser reactor containing a processing chamber with a constant liquid flow and optical monitoring path.

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## Preparation of nanoparticles by vacuum deposition on the ionic liquid surface

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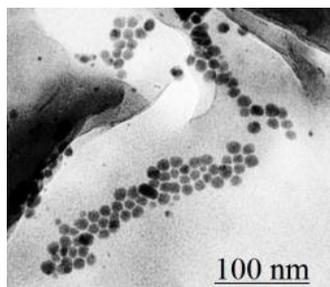
Room temperature ionic liquids (RTILs) are utilized in chemistry already for many years (“Green chemistry”) but in the field of physics or materials science their application is still rare. In 2006, the first experiment utilizing an exceptional property of RTILs – very low vapour pressure of about  $10^{-11}$  mbar – was performed by Torimoto et al. [1]. By sputtering they obtained a colloid with Au nanoparticles. We used the same procedure in preparation of magnetic nanoparticles of Ni and Ni-Fe in several RTILs (consisting of EMIM or BMIM cations and BF<sub>4</sub> or PF<sub>6</sub> anions). The main motivation was to prepare colloid with magnetic nanoparticles to be used later in sensorics. The further goal is to deposit proper nanoparticles from the nanocolloid to the thin-film gas sensor [2] in order to increase its sensitivity and/or selectivity.

The metals were deposited in UHV machine from two magnetrons onto ionic liquid poured in a Petri dish. The nominal composition of NiFe alloy was 80:20 which corresponds to that of permalloy. The presence of nanoparticles in the colloids was revealed by three different techniques: TEM, XRD, and UV-vis spectrometry (LSPR effect). We found the size of nanoparticles to be RTIL-dependent. For example, the nanoparticles formed by sputtering of Ni-Fe or Ag-Cu materials on the surface of the 1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide RTIL are several times larger than those formed by sputtering on the surface of EMIM-BF<sub>4</sub>. Even in that case they remain clearly faceted which is the property important for enhanced sensing and catalysis.

In our opinion, this novel technique provides an easy way for preparation of nanoparticles with narrow size distribution and of different complex composite materials (metallic, semiconducting or insulating) that cannot be prepared by chemical means. The nanocolloids are stable for many months, the nanoparticles inside are protected against oxidation, etc. At present, the deposition of the nanoparticles on a substrate is studied.

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*TEM micrograph of Ni-Fe (80:20) nanoparticles obtained by sputtering of Ni and Fe on the surface of the ionic liquid 1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide.*

*Average size of the **faceted** nanoparticles is about 12 nm.*

*Please note the self-assembling in a small area of the a-C substrate.*

## Progress in chemical methods of nanomaterials preparation

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The properties of nanomaterials are determined by a set of parameters, such as composition, size, shape, morphology, and structure. By tuning these parameters, the properties of nanomaterials can be tailored to enhance their performance in a particular application. Despite the enormous success over the controlled synthesis of nanomaterials with specific properties, all synthetic ways are in a very early stage of development.

In previous years, a large number of synthetic methods have been developed for generating of nanomaterials. Compared to organic synthesis of molecules where one can design and synthesize their endless number toward complex structures and functions, controlling the assembly of atoms into nanomaterial is still at a rudimentary stage. Interestingly, the chemical reactions involved in syntheses of nanomaterials often appear to be fairly simple. Strategies for preparation of precise structure and atomic composition in nanomaterial are dependent on the number of atoms in such materials. There are three distinct types of nanomaterials composed from the inorganic atoms within the core - nanoclusters, nanoparticles and assembled materials with nanostructured details. Nanocluster core is composed with the small number of atoms from one to less than 100 units with the diameter up to 3 nm. Nanoparticles are composed with the thousands atoms in the interval between 3 nm and hundreds of nm in different 3D orientations. Assembled materials with nanostructured details are complex systems with size exceeding micrometers.

The basic roles for precise units preparations of mentioned three types of nanomaterials play surface interactions between different cores of synthesized nanomaterials as well as surrounding liquids. This presentation outlines some problems engaging the different procedures for synthesis and separations of nanomaterials with precise composition, shape and structure.

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# Biological production of metallic nanoparticles

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In recent years scientists are inspired to develop new biosynthesis protocols for the fabrication of nanoscale metallic materials by use of different types of biomass. The biosynthetic method of metallic nanoparticles preparation can represent a relatively cheap, cost-effective and eco-friendly process and can contribute to the further development of modern nanotechnology.

Biosynthesis is very specific, due to the fact that it takes place either intracellularly or in a complex system of cell metabolites outside the cells. The complex system inside any living cell contains thousands of different molecules (proteins, polysaccharides, polyphenols, etc.) with varied functional groups (e.g. amine, hydroxyl, thiol, carboxyl, etc). These functional groups can be involved in redox processes of metal reduction. Biosynthesized nanoparticles are therefore mixed and stabilized with the complex system of cell debris containing metabolite products and biomolecules. This mixture is unique for any process of biosynthesis and can affect the properties of the biosynthesized nanoparticles.

In this abstract the preparation of diatom-bionanogold composite is briefly introduced. This composite is formed as a result of diatom cells *Diademesmia gallica* incubation in the presence of  $Au^{3+}$  ions. After bioreduction the biomass with biogold can be dried (Fig. 1), further modified (Fig. 2) or directly applied for example as a catalyst. Chrysophytes are also extremely interesting microorganisms with silica-based structures and *Mallomonas kalinae* cells were also used for biosynthesis of gold (Fig. 3). Fabrication of nanoparticles in the presence of siliceous structures provides occasion for novel bionanocomposite formation and their further use in numerous interesting applications.

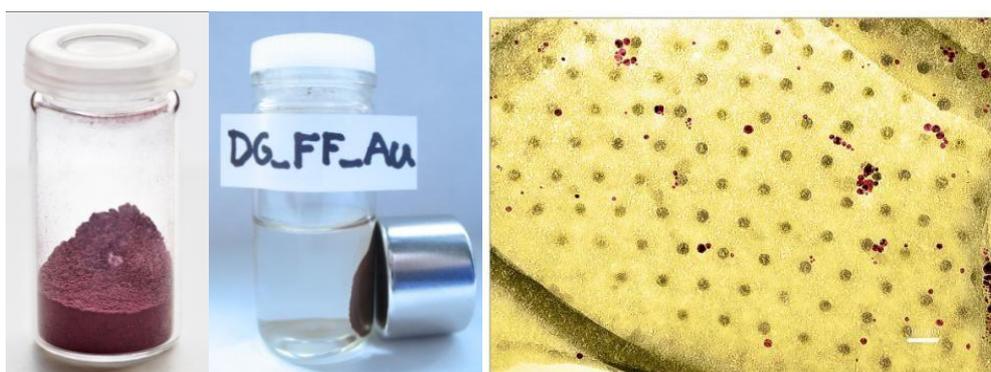


Fig. 1

Fig. 2

Fig. 3

Fig 1.: Bionanocomposite formed by *Diademesmia gallica* (DG) frustules and nanogold

Fig 2.: Magnetic modification of bionanocomposite kindly realised in the cooperation with Ivo Šafařík team from ASCR České Budějovice

Fig 3.: Detail of the siliceous structure of *Mallomonas kalinae* with gold nanoparticles (TEM picture kindly provided by Ivo Vávra and coloured by Vladimír Půlpán)

Acknowledgement:

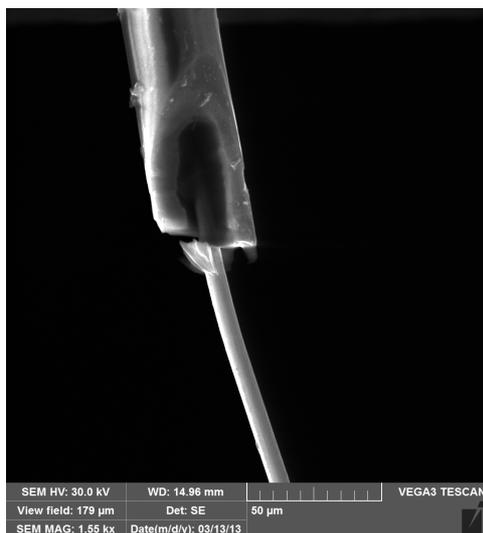
Nanotechnology – the basis for international cooperation project,  
reg. No. CZ.1.07/2.3.00/20.0074 SGS project No. SV 7303311/2101

# Nanocrystalline microwires for sensoric applications

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Amorphous glass-coated microwires are ideal materials for new, modern microsensors [1,2]. They are prepared by simultaneously drawing and quenching of molten master alloy. Method of preparation is well known as Taylor-Ulitovsky technique. Due to their preparation process, they are composite materials that consist of metallic nucleus (100 nm-20  $\mu\text{m}$ ), which is covered by Pyrex glass-coating of thickness 1-20  $\mu\text{m}$ . Due to their



amorphous structure and small dimensions, their magnetic properties are mainly driven by magnetoelastic and shape anisotropy. Therefore domain structure of microwire consists of one single mono-domain in the center of the wire with axial magnetization which is surrounded by the thin radial domains. Hence, microwires with positive magnetostriction are characterized by magnetic bistability due to their magnetization process that runs through the single large Barkhausen jump when the external field exceeds the so-called switching field,  $H_{SW}$ . The switching field is sensible to the temperature, mechanical stress, magnetic field, which gives us opportunity to employ the microwires as a sensor of the above mentioned parameters.

In the given contribution, basic magnetization process of amorphous and nanocrystalline microwire will be described. The velocity of the propagating domain wall in glass coated microwire is quite high (18 km/s) [3,4]. The origin of such fast domain wall will be explained and subsequently possibilities of different applications for sensing external parameters by microwires will be given.

Finally, the advantages of nanocrystalline microwires will be introduced showing fast and stable domain wall dynamics (in comparison to amorphous one) [5,6].

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## Magnetic processing of amorphous and nanocrystalline alloys

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The continuing interest in Fe-based amorphous and nanocrystalline alloys is motivated mainly due to their ability to combine a high saturation magnetic flux density with good magnetic softness. In order to further optimize the magnetic performance of these alloys it is important to deepen knowledge about the influence of the processing techniques that can be used to tailor their properties for specific applications. One possible way, which can be employed for this purpose, is the thermal processing under the presence of external magnetic field, called also „magnetic annealing“. A special attention of our work is devoted to the study of the effects of the magnetic annealing in order to produce a controllable anisotropy in the series Fe-Co-Nb-B, Fe-Co-B-Cu and Fe-Ni-Nb-B amorphous and nanocrystalline ribbons with different ratios of Fe/Co and Fe/Ni atoms. We show that the specimens annealed without the presence of external magnetic field show an appreciable increase of the coercivity and the corresponding hysteresis loops often exhibit a presence of steps due to the depinning of domain walls from the positions stabilized during annealing. After annealing in transverse magnetic field one can obtain sheared loops with tunable slope and good field linearity. A heat treatment under the presence of longitudinal magnetic field results in squared hysteresis loops characterized by the low coercivity values. Examples of our recent work on the tuning of soft magnetic properties in amorphous and nanocrystalline alloys for energy and sensor applications will be briefly highlighted.

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## Fundamental aspects of magnetooptics

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The Yeh's formalism based on 4 x 4 matrix algebra covers the most of the situation considered so far in magneto-optics. It is capable of treating the interfaces between two magnetic media and the structures containing such interfaces with no restrictions on the orientation of the magnetizations and crystalline axes at an arbitrary angle of incidence. The Kerr magneto-optical effects for general magnetization direction are summarized and the following three basic configurations are analyzed – polar, longitudinal, and transverse geometry. The Kerr effects in reflection are related to basic magneto-optical effects in transmission. Linear Faraday and quadratic Voigt effects are discussed in detail and the permittivity tensors are presented. Through the extension of the Yeh's matrix formalism to magnetic crystalline media the magneto-optic formulae in layered structures with magnetic ordering were obtained. The matrix formalism is an extremely useful form of the steady-state solution to Maxwell's equations subject to the boundary conditions imposed by isotropic and anisotropic multilayer stacks.

The characteristic matrices are derived for structures with magnetic ordering for linear magneto-optical (MO) effects. On the basis of these matrices the total matrix  $M$  describing the global reflection and transmission properties of system is specified. For the case of the prism, coupling gap, and single anisotropic film on the substrate the matrix  $M$  can be expressed as

$$M = (C^{(P)})^{-1}(D^{(P)})^{-1}D^{(0)}P^{(0)}(D^{(0)})^{-1}D^{(1)}P^{(1)}(D^{(1)})^{-1}D^{(2)}C^{(2)} = (C^{(P)})^{-1}(D^{(P)})^{-1}S^{(0)}S^{(1)}D^{(2)}C^{(2)},$$

where  $S^{(0)}$ ,  $S^{(1)}$  are the characteristic matrices of gap and film, respectively. Electromagnetic field on each boundary (prism-gap, gap-film, film-substrate) is obtained using the following partial products

$$M^{(P0)} = (D^{(P)})^{-1}D^{(0)}, M^{(01)} = (D^{(0)})^{-1}D^{(1)}, M^{(12)} = (D^{(1)})^{-1}D^{(2)}.$$

The reflection and transmission coefficients are expressible in terms of the elements  $M_{ij}$  of overall transfer matrix  $M$ .

The inspection of the wave equation at transverse configuration in uniformly magnetized media indicates that at the propagation vector  $\mathbf{k}$  orientation perpendicular to magnetization  $\mathbf{M}$  two mode pairs exist; each pair involves one mode for the forward propagation and the other one for the backward propagation. One pair is linearly polarized with the electric field vector parallel to  $\mathbf{M}$ . The second one is polarized predominantly perpendicular to  $\mathbf{M}$  with a small component parallel to the  $\mathbf{k}$  direction.

## Nanomaterials and amyloid aggregation of proteins

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Protein amyloid aggregation formed by the noncovalent polymerization of misfolding protein molecules is associated with pathogenesis of a group of human disorders known as amyloidosis including Alzheimer's disease or diabetes mellitus. The precise mechanism of toxicity of amyloid aggregates is not fully elucidated; however, there are evidences that prevention or reversion of the amyloid aggregation is beneficial.

Recently, the increasing attention is devoted to the study of the effect of nanoparticles on protein amyloid aggregation. We concern our study to investigate the *in vitro* anti-amyloid activity of magnetite nanoparticles, namely their ability to inhibit amyloid fibrillization and/or to destroy amyloid fibrils using several spectroscopic and microscopic techniques.

We have found that studied nanoparticles interfere with protein amyloid aggregation differently and final impact results from various nanoparticle properties such as the composition, size, surface charge or their coating with biocompatible molecules as bovine serum albumin (BSA) or dextran. The obtain data suggest that magnetite core of nanoparticles plays important role in their anti-amyloid activities. Moreover, our experiments showed that BSA modified magnetite nanoparticles significantly improved the cell viability, which was extensively reduced in presence of amyloid fibrils.

We assume that present findings make effective nanoparticles of potential interest for solution of the problems associated with protein amyloid aggregation.

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# Nanomaterials in catalysis

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Catalysis can play a prominent role in providing real solutions of the global concerns around of energy generation, green chemistry and CO<sub>2</sub> capture. Industry as well as academia display considerable and steadily increasing interest in using and further developing of highly active and selective catalysts.

Although the participation of catalysts on the price of the chemical product is only 1 - 4 %, the commercial success strongly depends on the selectivity of catalytic processes since the attainment of high selectivity to the desired product means that there is less waste produced.

A very broad and important group of heterogeneous catalysts is based on nano-scaled materials, e.g. metals, metal oxides, metal carbides which are usually deposited on structured supports with specified acid-base and textural properties. The combination of such properties allows designing multifunction catalysts. The general purpose of catalysts is to increase the rate of a given reaction. The advantage of nano-catalysts against conventional catalysts is that their extremely small size (typically 5-50 nm) yields a tremendous surface area – to – volume ratio which is in favor of chemical reactions. Also, when molecules are fabricated on the nanoscale, they achieve properties not found within their macroscopic counterparts.

This presentation covers information related to a general background with respect to structured nanosized catalysts and recent progress in preparation and commercial application of nano-materials in catalysis and chemical technology.

## **Surfaces of complex intermetallic compounds as selective hydrogenation catalysts**

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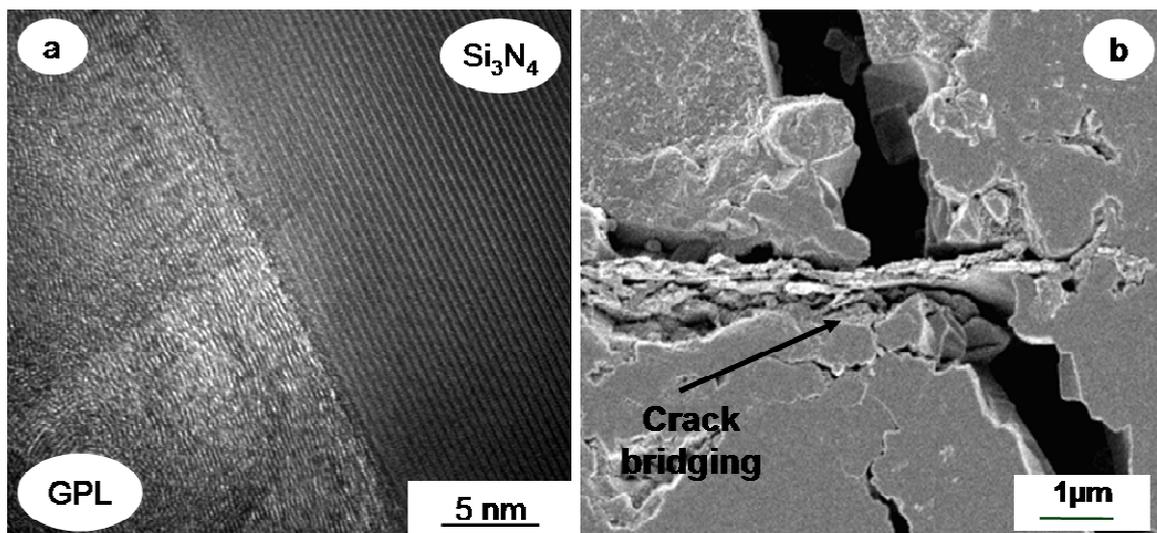
Surfaces of transition metals (TM) are effective catalysts for oxidation and hydrogenation reactions. The possibility to use for catalysis instead of the surfaces of close-packed TMs the surfaces of complex intermetallic compounds is a new promising and so far largely unexplored research area. While surfaces of the close-packed metals, as e.g. Pd(111), have only a few inequivalent adsorption sites, the surfaces of complex intermetallics provide a rich variety of different adsorption sites, leading to a multitude of possible reaction channels for catalytic reactions. The potential of using the complex intermetallic compounds for catalysis is here demonstrated on a model reaction - the selective semi-hydrogenation of acetylene. Recently it has been shown that some intermetallic compounds as Al<sub>13</sub>Co<sub>4</sub> or AlPd provide excellent activity and selectivity for the acetylene hydrogenation. Our works on Al<sub>13</sub>Co<sub>4</sub>, and AlPd compounds demonstrated that the catalytically active surfaces in both cases are surfaces with the (pseudo)five-fold symmetry. Ab-initio DFT calculations have been used to determine the atomic structure of the surfaces, to identify the reaction centers, to construct a detailed atomistic scenario for the hydrogenation reaction and to understand the activity and the selectivity of the catalysts.

# Silicon nitride + graphene platelet nanocomposites

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Silicon nitride + graphene platelet composites have been prepared using different volume fraction of various graphene platelets (GPL) and several processing routes; hot isostatic pressing (HIP), gas pressure sintering (GPS) and hot pressing (HP). Different methods have been used for the characterization of starting GPLs and the bulk microstructures; SEM, TEM, HRTEM, XRD, Raman spectroscopy, ESCA, AFM. The influence of the processing route and graphene platelets addition on the microstructure development, fracture characteristics, mechanical properties and functional properties has been investigated. The matrix of the composites prepared by GPS consists of  $\text{Si}_3\text{N}_4$  grains with smaller diameter in comparison to the composites prepared by HIP. The applied processing routes influenced significantly the final properties, e.g. the indentation fracture toughness of the composites was in the range  $6.1 - 9.9 \text{ MPam}^{0.5}$ , which is significantly higher compared to the monolithic silicon nitride  $6.5$  and  $6.3 \text{ MPam}^{0.5}$ . The highest value of  $K_{IC}$  was  $9.9 \text{ MPam}^{0.5}$  in the case of composite reinforced by smallest multilayer graphene nanosheets, prepared by HIP. The composites prepared by GPS exhibit lower fracture toughness from  $6.1$  to  $8.5 \text{ MPam}^{0.5}$ . The toughening mechanisms were similar in all composites in the form of crack deflection, crack branching and crack bridging.



Clean boundary of the  $\text{Si}_3\text{N}_4$  and GPL (a) and crack bridging by GPL (b).

# Nanocrystalline superhard coatings

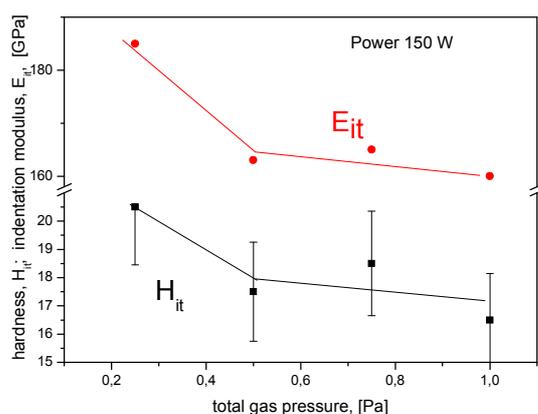
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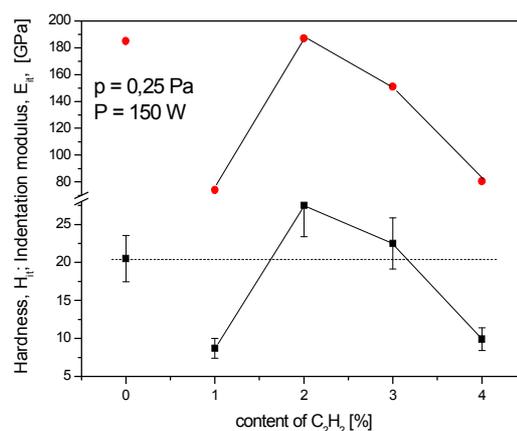
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The introduction of nanocomposite structures into thin coatings may result in significant increase of their hardness and elastic modulus. In the case of nanocomposite WC grains distributed in the matrix of carbon, high hardness can be theoretically achieved simultaneously with low coefficient of friction (COF). However, obtaining nanocomposite structures strongly depends on the ratio between hard WC and soft C phase. Conventional DC magnetron sputtering from WC target results in sub-stoichiometric nanocomposite WC<sub>1-x</sub> coatings. Carbon co-sputtering or reactive magnetron sputtering with carbohydrate gases are therefore used to control carbon content. Our earlier studies on PECVD WC-C coatings resulted in hardness of 28.4 GPa and COF ~0.11. The aim of the current work is to optimize the deposition conditions of DC and high power impulse magnetron sputtered (HiPIMS) WC-C coatings from the viewpoint of achieving high hardness.

The total gas pressure during deposition from WC target in pure Ar atmosphere optimized for high hardness was found to be <0.5 Pa (Fig. 1). The optimum addition of acetylene into Ar atmosphere was 2% and resulted in the hardness of ~26 GPa. The highest hardness of only 13.1 GPa was obtained with 2.5 % of C<sub>2</sub>H<sub>2</sub> added into Ar under the total pressure of 0.5 Pa during HIPIMS. Further optimization of HIPIMS deposition conditions is necessary due to increased number of deposition parameters.



**Fig. 1** The effect of total pressure of Ar on nano-hardness and indentation modulus of W-C coatings.



**Fig. 2** The dependence of hardness and Young's modulus on C<sub>2</sub>H<sub>2</sub> content.

**Acknowledgments:**— This work was supported by the projects APVV 0520-10 and VEGA 2/0108/11. The contribution of M. Ferdinandy, P. Horňák, P. Hviščová and M. Novák is acknowledged.

# Development and characterisation of Si<sub>3</sub>N<sub>4</sub>-SiC ceramic nanocomposites for high temperature applications

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Silicon nitride (Si<sub>3</sub>N<sub>4</sub>) based ceramics are prime candidates for such diverse high-temperature applications items as rotors and stator vanes for advanced gas turbines, valves and cam roller followers for petrol and diesel engines. In addition, silicon nitride is used for a variety of structural applications such as cutting tools of non-ferrous metal materials and ball bearings. However, the applications of silicon nitride based ceramics still require the improvement of their mechanical properties and long-term reliability. The improvement can be achieved through the control of factors such as phase composition of the starting powders, type and amount of sintering additives, processing parameters. Therefore, there is still a challenge for material researchers to improve the mechanical properties of silicon nitride ceramics by changing some of these parameters or by development of a new kind of composite materials.

The main aim of the work is to contribute to the further improvement of mechanical properties and reliability of silicon nitride based ceramics. The influence of various rare-earth oxide sintering additives and addition of silicon carbide particles into the silicon nitride matrix on the microstructure evolution and mechanical properties of silicon nitride have been investigated. The main challenge of the work is to find out a rare-earth oxide additive for silicon nitride-silicon carbide composite providing the best combination of mechanical properties at room and high temperatures. The composites contain SiC particles which are located either intragranularly, with a size of approximately 30-40 nm, or intergranularly with a size of approximately 150-170 nm. SEM and TEM observations revealed the different preferential locations of SiC particles in the Si<sub>3</sub>N<sub>4</sub> matrix with the changing of the rare-earth additives. It has been found out that the liquid phase with lower viscosity (larger ion of RE<sup>3+</sup>) tends to form intragranular SiC particles whereas the higher viscosity (smaller ion of RE<sup>3+</sup>) promotes the formation of intergranular particles of SiC. This finding is considered as the most important result because it has been proved that the nanoparticles at the grain boundaries are favourable for mechanical properties, especially at high temperature. The SiC nanoparticles hinder the grain growth of Si<sub>3</sub>N<sub>4</sub> resulting in finer microstructure and improved hardness, elastic modulus as well as the wear resistance. In addition, they serve as the obstacles for cation diffusion and grain boundary sliding leading to the higher oxidation and creep resistance.

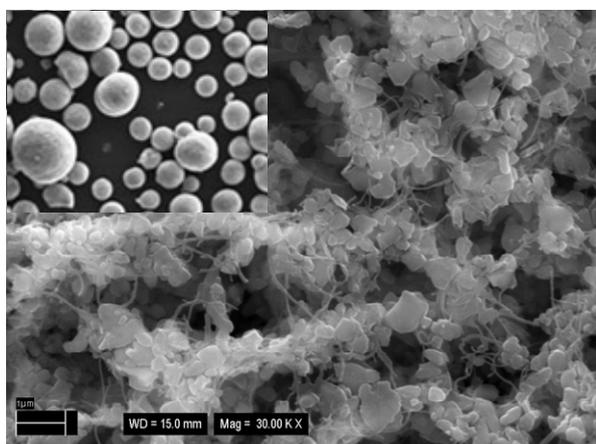
It can be concluded that the best combination of mechanical properties at room and high temperatures has been observed for the Si<sub>3</sub>N<sub>4</sub>-SiC micro/nano composite sintered with Lu<sub>2</sub>O<sub>3</sub>. Its superior mechanical properties are related to the following two effects: the presence of SiC particles located predominantly at the grain boundaries and presence of beneficial Lu-based grain boundary phase.

## Processing and properties of Al<sub>2</sub>O<sub>3</sub>-CNT and SiC-CNT nanocomposites

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Alumina (Al<sub>2</sub>O<sub>3</sub>) and silicon carbide (SiC) are extensively utilised structural ceramics, where low density, high hardness, chemical inertness and good high-temperature properties are required. However, both ceramics are brittle with poor fracture toughness and low thermal and electrical conductivity and thermal shock resistance. Carbon nanotubes (CNTs) can improve all the mentioned properties, however, it is very difficult to distribute them homogeneously in the ceramic matrix. In this work two approaches were used for the homogeneous distribution of multiwall CNTs: a) freeze granulation of the CNTs containing suspension; b) in situ preparation of CNTs in the ceramic green body by catalytic CVD process. The first new approach comprises the functionalization of MWCNTs by acid treatment, stabilization of Al<sub>2</sub>O<sub>3</sub>/MWCNT dispersion with subsequent freeze granulation, which retains the homogeneity of the aqueous suspension in the ceramic green bodies (Fig. 1).



**Fig. 1.** Granules of Al<sub>2</sub>O<sub>3</sub>/CNT composite powder and detail of granule surface with CNTs.

In the second approach (CVD) the SiC powder was coated with Fe<sub>2</sub>O<sub>3</sub>, which catalyzed the growth of CNTs by CVD from C<sub>2</sub>H<sub>2</sub>. After optimization we have succeeded to prepare a ceramic green bodies with homogeneously distributed CNTs. Both Al<sub>2</sub>O<sub>3</sub>-CNT and SiC-CNT composites were densified by hot-pressing at 1550°C (Al<sub>2</sub>O<sub>3</sub>) and 1800°C (SiC) in argon atmosphere and 30 MPa load. Microstructural analysis as well as electrical conductivity measurements has been used for observation of distribution of nanotubes within composites.

The electrical conductivity of (Al<sub>2</sub>O<sub>3</sub> + 10 vol% CNT) composite, as an indicator of homogeneity of conductive network distribution, increased from 6 to 1140 S/m when compared the conventional process and freeze granulation approach. Moreover, homogeneous distribution of CNTs resulted in the refinement of microstructure measured with respect to the average grain size of alumina particles (~1 μm) compared to conventional powder mixing (~5 μm) at the same CNTs loading. The fracture toughness of Al<sub>2</sub>O<sub>3</sub>-CNT composites increased to 5.5 MPa·m<sup>1/2</sup> in comparison to 3.3 MPa·m<sup>1/2</sup> for pure alumina.

Similar improvement of properties was achieved also for the SiC-CNT nanocomposites. The electrical conductivity was increased to 4370 S/m, while retaining the good fracture toughness 5.3 MPa·m<sup>1/2</sup> and hardness 20.7 GPa.

## **Development and mechanical properties of ZrO<sub>2</sub> ceramic nanocomposites reinforced by boron nitride nanotubes**

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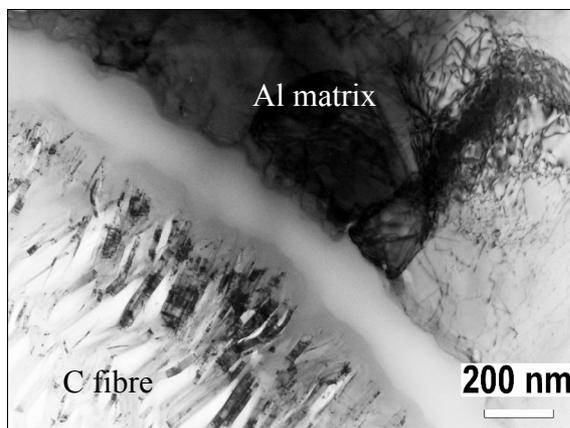
Boron nitride nanotubes (BNNTs) are a new style of reinforcements because they are found to be as strong, flexible and elastic as carbon nanotubes (CNT), however the superiority of BNNT is their good thermal and chemical stability and high oxidation resistance up to 900°C in air. Hollow “cylindrical” and “bamboo-like” structured boron nitride nanotubes have been used to reinforce tetragonal yttria stabilized zirconia ceramics (ZrO<sub>2</sub>) via spark plasma sintering (SPS). Different amounts of the BNNTs (0, 0.5, 1, 2.5 and 5 wt.%) have been incorporated into the ZrO<sub>2</sub> matrix for preparation of the composite systems. The zirconia grain size increased with increasing amount of the BNNTs as the BNNTs promoted the densification process due to the presence of metal catalysts. Elastic modulus of the materials decreased with increasing amount of the nanotubes. On the other hand, the hardness first increased after addition of 0.5 and 1 wt.% of the nanotubes and then decreased with further increasing amount of the nanotubes. The fracture toughness increased continuously with increasing amount of nanotubes up to 2.5 %. Thus, the incorporation of 2.5 wt.% of BNNTs into the 3Y-TZP zirconia resulted in the increased fracture toughness by ~100 % compared to the reference monolithic zirconia. Moreover, the fracture toughness significantly increased even after addition of small amount of BNNTs (0.5 and 1 wt.%) reaching an improvement in the range of 72 - 85 %. Toughening mechanisms resulting from the incorporation of boron nitride nanotubes have been examined thoroughly by SEM observations of the composite fracture surfaces and by investigation of crack propagation after Vickers indentation. BNNTs bridging cracks, accompanied by stretching of the nanotubes, have been observed during the crack propagation as the toughening mechanisms. The pull-out lengths of the BNNTs were determined to be in the range from 0.5 to 2.4 μm, regardless the type of nanotubes structure as well as the BNNTs content in the composites. The introduction of BNNTs strengthened the grain boundaries, which seems to be more important and dominant mechanism than pull-out. Moreover, the addition of BNNTs promoted the transformation toughening effect as the result of the larger grain size effect. BNNTs directly toughened the zirconia matrix only at low content where the transformation toughening can be neglected, resulting in an improvement in fracture toughness up to 85 %. On the other hand, the transformation toughening simultaneously accompanied by the toughening effect of the nanotubes are responsible for the highest fracture toughness of the composite with 2.5 wt.% BNNTs.

## Metal matrix composite materials – structure and interfaces

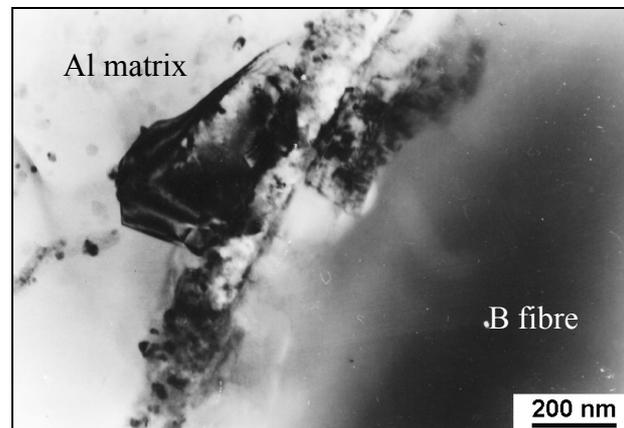
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Review of metal matrix composite materials developed and studied for nearly 6 decades at the Institute of Materials and Machine Mechanics of the Slovak Academy of Sciences will be presented. Particular attention is paid to various technologies used for their preparation, *e.g.* diffusion bonding, gas pressure infiltration, air plasma spraying and hot isostatic pressing. Composite materials with aluminium, copper, magnesium, steel and silicide matrices reinforced with fibres, particles and ceramic preforms are presented.



TEM micrograph revealing amorphous layer at the fibre matrix interface in Al/C composite



TEM micrograph with continuous reaction layer at the fibre – matrix interface in Al/B composite

Composites as structural materials as well as materials with specific physical properties are discussed.

Special attention is devoted to the role of structure and interfaces on their properties. Various microscopic techniques used for structural studies will be reminded. The importance of interface analysis down to nanometric scale will be presented.

## Preparation of metallic nanoparticles by selective leaching

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Nanocrystalline metals are very promising materials both in form of nanoparticles and also as bulk materials. The production of such materials is usually limited by small amount of prepared metals and alloys. One of the possible ways of industrial production is selective leaching. This technique lays in preparation of supersaturated solid solution of desired element in matrix metal – by convenient heat treatment or by rapid solidification of the binary alloy. Consequently, the matrix metal is selectively dissolved and metal nanoparticles from other metal are formed. The size, shape and agglomeration of forming metallic nanoparticles are dependent on many factors such as reaction temperature, concentration of leaching solution, additives present in leaching solution.

In our research we use mainly aluminium matrix. The reason for this is amphoteric behaviour, which enables aluminium dissolution in sodium hydroxide without affecting the minor metal. Nobel metals like silver or copper forms monocrystalline nanoparticles and their size is dependent on temperature (increasing with increasing temperature). Nickel forms polycrystalline sub-micrometer particles which grain size is dependent on temperature as shows Fig. 1. Formed nanoparticles exhibit massive agglomeration. It is not limitation of the process, because the application of nanoparticles is as a precursor for production of bulk nanocrystalline materials (metals, alloys and metal matrix composites). Compaction of nanoparticles prepared by selective leaching is possible by several methods; the most suitable seems to be spark plasma sintering.

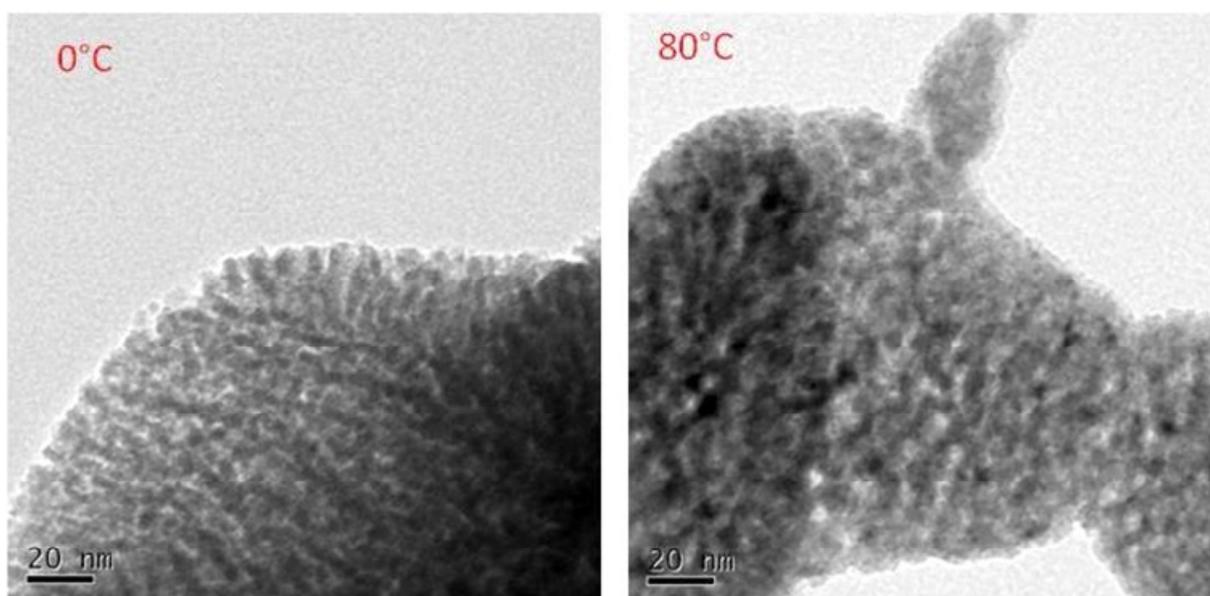


Fig. 1. Structure of Ni nanoparticles prepared at temperatures of 0°C and 80°C

## Formation of nanoparticle arrays by self-assembly

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Self-assembled nanoparticle arrays play ever increasing role in pushing the frontiers in nanoelectronics, nanooptics, spintronics, sensors and other fields where tailoring special properties at nanoscale is crucial. Van der Waals attraction, steric repulsion, dipole-dipole interactions and adhesion to a substrate are the main forces governing the self-assembly when a drop of a nanoparticle colloidal solution is applied on a solid substrate. A 3D ordered nanoparticle array is formed during the solvent evaporation provided the nanoparticles are monodisperse in size. Alternatively, 2D ordered nanoparticle arrays at the air/water interface are prepared in a Langmuir-Blodgett (LB) trough and transferred onto a substrate, following the technique known from the molecular thin films. It is essential to elucidate details of the self-assembly process in order to prepare nanoparticle arrays in a controlled manner and to achieve desired nanoparticle array functionalities.

The contribution presents a real-time study of the silver nanoparticle self-assembly at the air/water interface by the grazing-incidence small-angle X-ray scattering (GISAXS) completed by Brewster microscopy, imaging and null ellipsometry and atomic force microscopy. The spherical nanoparticles with metallic core of the  $7\pm 0.7$  nm diameter and a surfactant shell (oleic acid and oleylamine) to prevent agglomeration were prepared by inverse micelle technique. The nanoparticles exhibit plasmon resonance close to 500 nm. The GISAXS measurements were performed at ID10B beamline at ESRF, Grenoble, with a fast 2D X-ray detector PILATUS 300K tracking immediate response to the barrier movement of the nanoparticle film compressed on the water surface in the LB trough. This enabled us to identify all principal self-assembly stages including those far from the equilibrium which were related to the surface pressure - area isotherm.

The formation of nanoparticle monolayer starts with coalescence of free self-assembled nanoparticle islands with the 2D hexagonal close-packed order inside (stage I). In stage II, the surface pressure starts to grow as the proceeding island coalescence forces the larger assemblies to get into contact. The stress accumulated at the assembly boundaries is partly relieved by the nanoparticle re-arrangements to form a continuous close-packed monolayer with local hexagonal order preserved from the original islands. The end of stage II is suitable for the transfer onto a solid substrate to deposit a high-quality nanoparticle monolayer over large area. In stage III, the accumulated stress accelerates the surface pressure growth and the elastic modulus goes to a maximum while the nanoparticle lattice gets temporarily squeezed by approximately 0.1 nm and the lattice disorder increases. This highly non-equilibrium phase preceding the monolayer collapse has never been observed before. The collapse (stage IV) takes place by flipping up some nanoparticles and the 2D-3D transition. The AB-like crystallographic stacking with enhanced paracrystalline disorder inherent to self-assembly was identified in the newly formed bilayer. The Langmuir film expansion runs irreversibly by decomposition into bilayer islands. The results obtained have direct implications for preparation of plasmonic nanoparticle templates.

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## Asymmetric Rolling as SPD Technology

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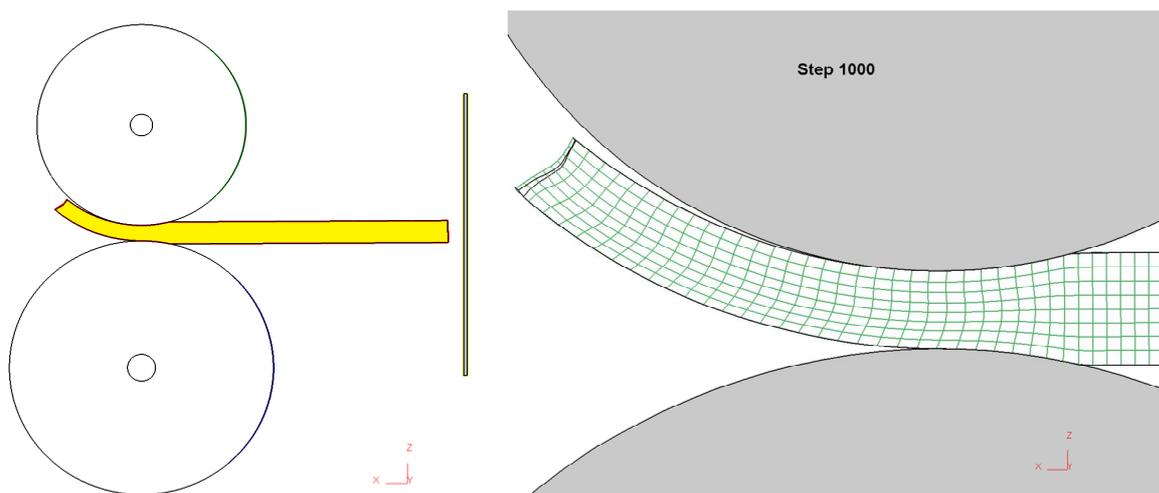
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The severe plastic deformation (SPD) methods should be divided from point of view length of processing material on discrete and continuous processes. The discrete processes are: high pressure and torsion (HTTP), multiaxial forging (MF) and all processes based on material extrusion and material bending. The continuous processes are based on rolling technique (equal channel angular rolling, rolling and axial rolls shifting, linear flow splitting, accumulative roll bonding and asymmetric rolling).

The asymmetric rolling (ASR) can be achieved on duo rolling mill with following technique: different roll's diameter ( $D_1 \neq D_2$ ), different roll's circumferential speed ( $v_1 \neq v_2$ ), different friction coefficient between material and rolls ( $f_1 \neq f_2$ ) and only one roll is driven.

A material processing by ASR technique will be discussed from point of view numerical simulations by SW Deform 3D and physical simulations realized on duo rolling mill (radius of working rolls:  $R_1=28,5\text{mm}$ ,  $R_2=36,0\text{mm}$ ,  $R_2/R_1=1,26$ ). The samples were processed with thickness deformations  $\varepsilon=30,24\%$  at ambient and  $\varepsilon=28,16\%$  at cryogenic temperature conditions. A cooper alloy CuCrZr was used as experimental material.

A numerical simulations of ASR with different roll's diameter ( $D_1/2=28,5\text{mm}$  and  $D_2/2=36,0\text{mm}$ ,  $f_1=f_2=0,6$ ,  $v_1=2,98\text{ m/s}$ ,  $v_2=3,77\text{ m/s}$ ) shown on asymmetrical material flow **Fig.1** and distribution of effective stress of rolling material which is given in **Fig.2**.



**Fig.1** Asymmetrical material flow of different roll's diameter ( $D_1 \neq D_2$ )

# Crystallization processes in NANOPERM-type nanocrystalline alloys studied by CEMS, CXMS, and NIS techniques

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Iron-based metallic glasses and their nanocrystalline counterparts are interesting for their high magnetic permeability and remanence. These properties are affected by the alloy's composition and the degree of the crystallization [1].  $^{57}\text{Fe}_{80}\text{Mo}_9\text{Cu}_1\text{B}_9$  and  $^{57}\text{Fe}_{75}\text{Mo}_8\text{Cu}_1\text{B}_{16}$  alloys were prepared by the method of planar flow casting on quenching wheel in a form of ribbons about 1 mm wide and 20  $\mu\text{m}$  thick. For the sake of our experiments, the alloys were prepared from iron enriched to the isotope  $^{57}\text{Fe}$  to about 50 %. The natural abundance of  $^{57}\text{Fe}$  is only 2.17 %. The as quenched samples were annealed at 510 and 550 °C during 30 min.

By using depth selective techniques of Mössbauer spectrometry we discuss the surface crystallization at both sides of ribbons. The methods of CEMS (*Conversion Electron Mössbauer Spectrometry*) and CXMS (*Conversion X-ray Mössbauer Spectrometry*) provide information from subsurface regions located at  $\sim 200$  nm and at  $\sim 1000$  nm, respectively. Mössbauer spectra of the identified nanocrystalline phases were refined by a wide distribution of magnetic hyperfine fields and narrow six-line subspectra. They describe interfacial regions, bcc-Fe, and  $\text{Fe}_3\text{O}_4$  crystals, respectively. The residual amorphous matrix was reconstructed by distributions of quadrupole doublets. Presence of  $\text{Fe}_3\text{O}_4$  (magnetite) was found mainly at the wheel side of the  $^{57}\text{Fe}_{80}\text{Mo}_9\text{Cu}_1\text{B}_9$  alloy in the near surface regions (CEMS) and less abundant in deeper layers (CXMS). At the air side, the presence of magnetite was confirmed only from the CEMS spectra. After annealing at 550 °C, the magnetite disappeared completely.

Bulk crystallization of the ribbons was investigated by NIS (*Nuclear Inelastic Scattering*) technique employing the 3<sup>th</sup> generation source of synchrotron radiation at the European Synchrotron Radiation Facility (ESRF) in Grenoble. Using NIS technique we have directly measured the phonon energy spectra. Density of phonon states (DOS) including vibrational properties were evaluated by the PHOENIX code [2]. By decomposition of DOS into components corresponding to the crystalline phase and to the amorphous rest we obtained their relative fractions in the bulk of the investigated alloys. All measurements were performed at room temperature.

This work was supported by the grants VEGA 1/0286/12 and SK-PL-0032-12 and it was performed as a part of the IAEA RC-1196.1 action entitled 'Utilisation of accelerator-based real-time methods in investigation of materials with high technological importance'.

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## Precession electron diffraction of fine-grained structures

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Amorphous alloy systems, usually prepared by rapid quenching of the melt, are as a rule thermally processed to maximize their physical properties, e. g. magnetic, or mechanical. Thermal treatment may either leave the structure in original amorphous state or transform it into a composite consisting of small crystalline grains with sizes ranging from a few to hundreds of nanometers embedded in remaining amorphous matrix. Determination of phases and orientation of the nanograins is, alongside with phase content quantification and size distribution, of major importance.

While in classical solids with grain sizes of micron or even submicron sizes this problem is solved by using electron backscattered diffraction (EBSD) in scanning electron microscopes (SEM), this method can be applied only with difficulties to smaller grains. Transmission electron microscopy (TEM), due to its high spatial resolution, is very convenient for imaging and analysis of nanocrystals. By forming a parallel beam in TEM and selecting a crystal with an aperture, or by forming a fine convergent beam of only a few nanometres diameter, electron diffraction (ED) pattern can be recorded from crystals too small to be studied by either EBSD or X-ray diffraction. The study of crystals at nanoscale or even atomic level by electrons – electron crystallography – is an important complement to X-ray crystallography. Among the main advantages of structure determinations by electron crystallography compared to X-ray diffraction are the facts that crystals several orders of magnitude smaller than those needed for X-ray diffraction can be studied.

Recently developed experimental technique reducing dynamical effects in electron diffraction data and thus allowing the use of ED pattern intensities directly for ab-initio structure determination is precession electron diffraction (PED) [1, 2, 3]. In this technique, the incident beam is precessed in a hollow cone around the central zone axis direction as the data are collected. The collected diffraction data show reduced dynamical effects because there are far fewer simultaneously excited reflections in the off-zone condition. In addition, the precession integrates the diffraction intensities through the Bragg condition, which provides data sets significantly less affected by minor sample tilts and makes interpretations of pattern symmetry more reliable.

The advantages of PED for identification and mapping of nanocrystalline phases will be demonstrated on crystallization of rapidly quenched Fe-Co-Si-B forming ~100 nm large grains of bcc-Fe(Co) dispersed in amorphous matrix.

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## TEM characterization of nanoparticles and their penetration into human cells

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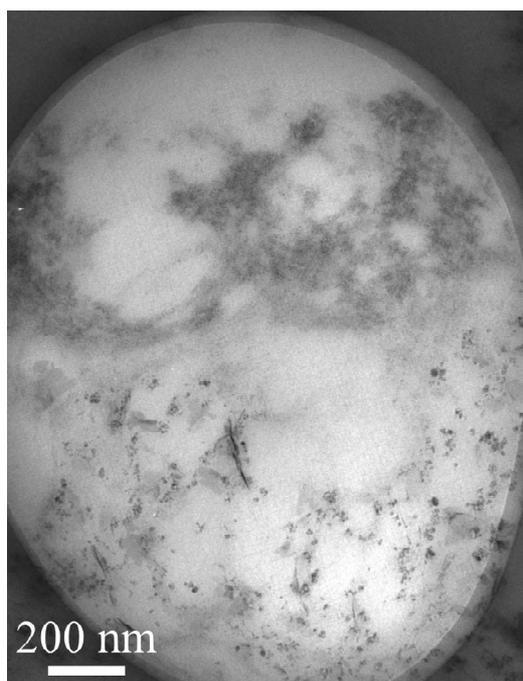
<sup>3</sup>*Slovak Medical University, Bratislava*

The technique of electron- microscopical characterization of nano-colloids containing various solid nanoparticles (NPs) prepared by different technologies (e.g. Fe<sub>3</sub>O<sub>4</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>) will be presented. The crystalline state of nanoparticles and their size distribution were determined.

In subsequent experiments the various human cells were influenced in-vitro by nanoparticles. The influenced cells were analysed by TEM on the specimens prepared by ultramicrotome. The distribution of nanoparticles penetrated in cells was determined by bright and dark-field microscopy.

We can conclude that the NP penetration in cytoplasm is relatively quick (Fig.1). We observed it in all experiments. The penetration into cell nucleus was not observed. Our microscopical results are in correlation with biochemical analysis.

For the safety NPs applications in any field it is necessary to know the detailed NPs structure including their surface structure. The NPs application without biochemical analysis in specific environment is risky.



*Fig. 1. The TEM micrograph of the cytoplasm/nucleus interface. The magnetite nanoparticles are distributed only in cytoplasm where they decorate the cytoplasm structures. The nucleus (upper part) is free of NPs.*



**Abstracts**

**Poster Contributions**



# **The effect of magnetite nanoparticles on cell signaling in the human tumor lung cells**

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Magnetite nanoparticles (MNPs) are increasingly being investigated for variety of biomedical applications, both diagnostic and therapeutic. MNPs have a great potential as contrast agents for magnetic resonance imaging (MRI), heat mediators in hyperthermal therapy and nanocarriers for targeted drug delivery. Moreover, the unique superparamagnetic properties allow delivery and trapping the drug-loaded MNPs in the target site *via* an external magnetic field. MNPs are coated with various synthetic or natural moieties to prevent aggregation and make them stable and biodegradable. Although MNPs are considered to be non-toxic, the impact of MNPs on basic cellular processes such as cell cycle, cell signaling, apoptosis, oxidative stress or inflammation is not sufficiently explored.

In this study we investigated the effect of nanospheric superparamagnetic magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$ , 7.6 nm in diameter) on cell signaling in human alveolar epithelial carcinoma cell line A549. Three types of MNPs were used in this study: MNPs coated with i) sodium oleate (SO prevents aggregation and makes MNPs stable), ii) SO + polyethylene glycol (PEG reduces interactions with plasma proteins and so minimizes their internalization and clearance by macrophages), and iii) SO + PEG + copolymer poly(lactic-*co*-glycolic acid) (PLGA prevents degradation and aids in regulation of drug release from nanoparticles). All MNPs were characterized in depth with different chemical and physical means. Here, we focused on mitogen-activated protein kinases (ERK1/2, SAPK), nuclear factor kappa B (NF- $\kappa$ B), p53 protein and caspase 3, the key proteins involved in growth, differentiation, immune and inflammatory responses and cell death regulation. The activity of these proteins were assessed under control and MNPs exposed conditions by Western blot and immunostaining. All MNPs regardless of the surface modifications induced a time-dependent increase in ERK1/2 and NF- $\kappa$ B activities in A549 cells compared with control cells. Our results indicated that MNPs may affect basic cellular processes.

Acknowledgement. This study was supported by VEGA grants 2/0051/09 and 2/0143/13.

# Reaction of Soman (GD) with suspensions containing gold and silver nanoparticles

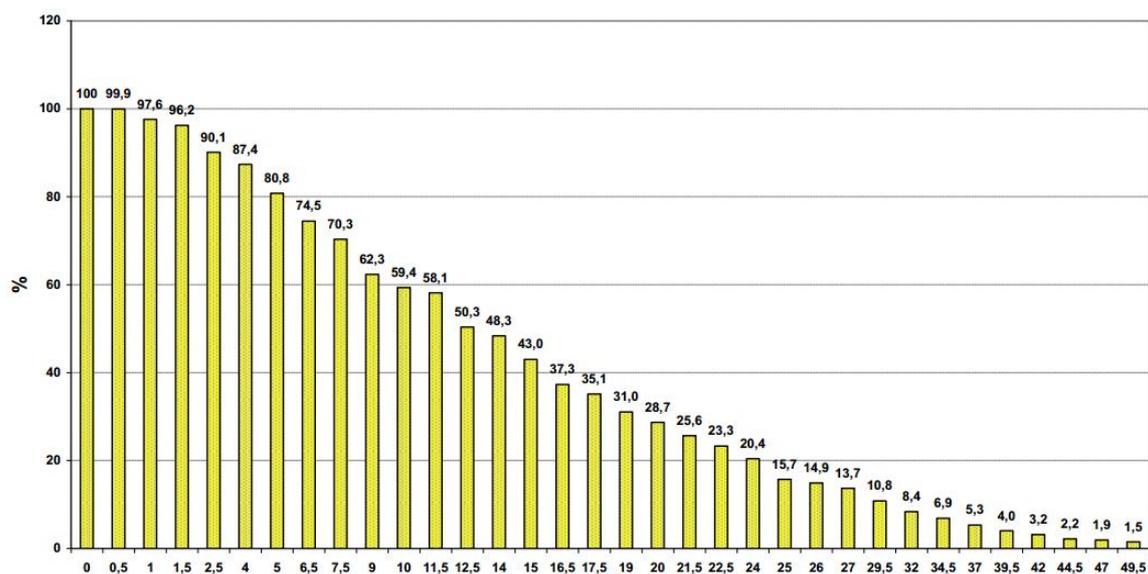
Veronika Holišová, Marta Natšínová

*Nanotechnology Centre, VŠB - Technical University of Ostrava, Czech Republic*

This work focuses on the biosynthesis of Au and Ag nanoparticles and their practical aspects. Gold and silver nanoparticles were successfully prepared by means of two algal strains (*Diadlesmis gallica* - DG and *Mallomonas kalinae* - MK) mixed with aqueous salt (HAuCl<sub>4</sub> for AuNP and AgNO<sub>3</sub> for AgNP) in laboratory conditions. The interaction of algae with aqueous salt promoted the precipitation of metal nanoparticles. In the case of MK contact with gold ions bioreduction of gold nanoparticles occurred very quickly - in the course of few minutes. Prepared nanoparticles were characterized by transmission electron microscopy.

Suspensions containing biomass and gold or silver nanoparticles were used as catalysts for the hydrolytic degradation of warfare agent Soman (GD). Experiments were kindly realised within the cooperation with The National Institute for Nuclear, Chemical and Biological Protection. 15 ml of the suspension was mixed in the headspace vial with defined quantity of GD. The progress of hydrolysis and concentration of GD was continually checked every 30 minutes.

The results showed a positive effect on the degradation of GD in suspension with gold nanoparticles. On the contrary, presence of biosilver increased stability of GD and the course of hydrolysis was slower in comparison with the control experiment. Catalytic degradation of soman was analyzed by gas chromatography/mass selective detector using the technique of direct–solid phase microextraction



The percentual decrease of GD concentration in the suspension MKAu during 48 hours.

Acknowledgement: The study is supported by the SGS project No. SV 7303311/2101.

# **Nanocomposites of polyaniline and inorganic nanoparticles prepared in ionic liquids.**

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Ionic liquids (ILs) are a new class of solvents attractive due to their unique combination of low volatility, chemical stability, high conductivity, wide electrochemical window, and tunable solvent properties. Synthesis and stabilization of nanocolloids is an emerging application of ILs [1]. Immobilization of nanoparticles on a sensor surface (e.g. for biochemical sensing) and preparation of nanocomposites belong to the main challenges.

Here we report on a method for synthesis of nanocomposites of conducting polyaniline (PANI) and inorganic nanoparticles dispersed in IL. ILs used in this study were based on imidazolium cation (BMIM) and inorganic anions (e.g.  $\text{BF}_4^-$  or  $\text{CF}_3\text{SO}_3^-$ ). First, metal-oxide nanoparticles ( $\text{TiO}_2$  or  $\text{ZnO}$ ) were dispersed in ionic liquid and aniline monomer was added into the solution. Second, using the electrochemical polymerization, PANI/nanoparticle nanocomposite was deposited directly on the surface of gold interdigitated electrodes fabricated on oxidized silicon substrates.

Chemical structure and morphology of nanocomposites were studied by FTIR spectroscopy and electron microscopy observations. Changes of the electrical resistance of the nanocomposites upon the exposure to ammonia and hydrogen gases were investigated. We found high and reversible response to the concentrations as low as several ppm indicating that PANI-based nanocomposites prepared in ionic liquid are applicable to gas sensors operating at room temperature.

[1] H. Wender, et al. *Coordin Chem Rev.* in press, doi:10.1016/j.ccr.2013.01.013 (2013).

## Compactization of soft magnetic materials with aluminium addition

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The main aim of the present work was to study the effect of compaction (compressibility) as well as physical properties (apparent and tap density) on the behaviour of a new development soft magnetic material - Insulated Iron Powder Compound (IIPC) with different addition of aluminium alloy.

IIPC are basically pure iron powder particles coated with a very thin electrically insulated layer. In this case the components made of metal powder cannot be sintered, as it is fundamental that each particle is electrically insulated from the other.

The main aim of this work is to study the effects of aluminium alloy addition as well as processing conditions on soft magnetic materials (SMM) behaviour in terms of magnetic properties.

The starting material was IIPC with an addition of 5 wt. % aluminium alloy (Al - 0.95 wt. % Mg - 0.49 wt. % Si - 0.21 wt. % Cu - 0.07 wt. % Fe). Particles size distribution was carried out by sieve analyzer according to ISO 4497. Powder mixtures were homogenized using a laboratory Turbula mixer for 1200 s<sup>-1</sup>. Specimens with a different green density obtained using a 2000 kN hydraulic press, in a disc-shaped mould ( $\varnothing 40 \cdot 10^{-3}$  m) and unnotched impact energy  $55 \times 10 \times 10 \cdot 10^{-3}$  m<sup>3</sup> specimens applying a pressure in the range from 200 to 700 MPa. Heat treatment was carried out in vacuum furnace at 773K for 1800 s<sup>-1</sup>. Densities were evaluated using the water displacement method.

Different stages during compaction were identified and overlapped in terms of particle rearrangement and plastic deformation.

The magnetic properties of investigated materials appear to be mainly controlled by the density. The remanence and coercivity increased with increasing density that is also attributed to the enhanced densification. However, the subsequent decrease of remanence and increase of coercivity are observed in terms of addition of aluminium alloys. The maximum values of coercivity (about 400 A/m) were attained mainly in case of higher compactive pressures; i. e. as consequence of the higher applied forces that cause a greater reduction of volumes and of present porosities, which typically results in a demagnetization field effect. Two factors are considered with respect to the mentioned results: the magnetic properties of the SMM are mainly influenced by density and “sintering” degree.

Acknowledgement:

This work was realized within the frame of the Operational Program Research and Development: “The centre of competence for industrial research and development in the field of light metals and composites“, project code ITMS: 26220220154 and financially supported by a European Regional Development Fund.

## **Possibilities of ECAP and ECAR in powder metallurgy area**

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The main preparation way of powder metallurgy (PM) aluminium alloys are presently conventional press-and-sintering methods. These methods are an inexpensive near net shape process, however very restricted because of the difficulties arisen from the extremely stable oxide layers that cannot be broken or removed by heating due to the thermodynamic stability, therefore failing to create the sintering contacts, which actually bear the load in the material. A possibility to overcome this problem is by means of liquid phase sintering (LPS), as well as the use of sintering additives on enhancing aluminium sinterability, especially in particles wettability. Nevertheless the presence of secondary porosity, as the one resulting from LPS, is the main problem. Less chemically stable oxide particles may be reduced during the sintering, nevertheless leave porosity behind. The same happens for voids left by lubricant agglomerates or alloy elements that are homogenized by transient liquid phase. The porosity can become a crucial indicator for the evaluation and control of the processes which the components underwent. Pores act as crack initiators; the distribution of stress is inhomogeneous across the cross section and reduces the effective load bearing area. Both the morphology and distribution of pores have a significant effect on the mechanical behaviour of PM materials, therefore their knowledge is very important.

In the past decade, the research focused on how to strengthen Al alloys via severe plastic deformation (SPD). Conventional forming methods are ineffective in the achieving of favourable properties area of produced parts, adequate to structural properties; moreover through them only limited levels of structural and strength-plastic characteristics can be obtained. The solution may be SPD methods. SPD may provide the possibility of porosity removal (mainly secondary), which have not been resolved yet in PM area.

The most widely used and the most widespread SPD method is ECAP (equal channel angular pressing). The ECAP offers a lot of advantages. On the other hand the main disadvantage of this method is connected to a small specimen size. ECAR (equal channel angular rolling) negate the mentioned disadvantage, due to the infinite longer specimens with ultrafine grained microstructure that can be obtained. By the ECAP method, the experimental material is pressed through a special die consisting of two equal channels at some angle (most frequently 90°) with the same cross-section. The cross-sectional area remains unchanged; the same sample can be pressed repetitively to attain exceptionally high strains. ECAR process is angle rolling through the same channel.

The main results is the identification and the convergence of the results between simulation and real ECAR process (Dpt. of Metals Forming, TU Košice will be the first researcher ECAR process in PM area). Moreover, the SPD processes can be useful for the determination of suitable combination of strength and plastic properties.

Acknowledgment: This work was financially supported by the projects: VEGA 1/0385/11.

## Vacuum deposition of metals onto liquid substrates

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Vacuum sputtering of various materials onto the surface of liquids with sufficiently low vapour pressure has been recognized as a suitable physical method of preparation of nanomaterials [1]. As opposed to chemical procedures, the physical methods are based on physical transformations of matter, which do not change the original chemical composition.

An ionic liquid (IL) is a salt in which the positive and negative ions are poorly coordinated, which enables this solvent to be liquid below 100°C. Since vapour pressure of some ILs can be as low as  $10^{-10}$  Torr, sputtering deposition onto ILs received significant attention over past few years. However, the exact mechanisms occurring at the liquid substrates are still relatively unknown.

To obtain deeper insight into these mechanisms, we performed a series of vacuum-deposition experiments using silicone oil, vane-pump oil and four different ionic liquids based on 1-Butyl-3-Methyl-Imidazolium (BMIM) cation as liquid substrates. Both RF magnetron sputtering and vacuum evaporation were used for deposition of gold or copper. Although in most cases Au film was deposited onto the surface of silicone oil, we found that with increasing power of magnetron the gold penetrated into the oil and we obtained reddish solution. Following this principle, metallic film was observed even on surface of IL after the evaporation of copper at low heating power of the source. We assume that the power delivered to the surface of the liquid by sputtered atoms, interaction with plasma or by IR irradiation (e.g. from the source of metal vapours) is the key parameter determining whether the metallic film or the solution of metal particles is obtained. We also found that appearance of some IL-based solutions changed during several hours after the deposition. This is an evidence of the ability of ILs to dissolve metallic species or disassemble aggregated particles.

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## Cross-sectional structural analysis of the nano-indent region in molybdenum nanoporous thin film

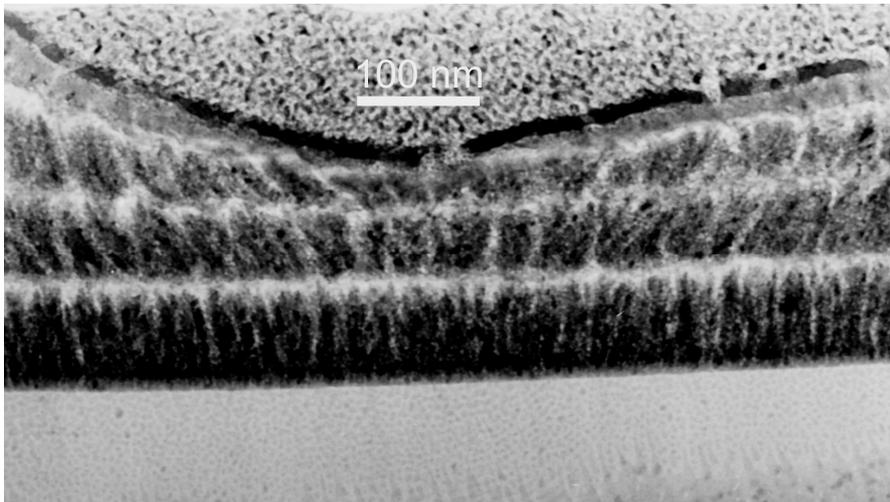
Šmatko V.<sup>1</sup>, Hvizdoš P.<sup>2</sup>, Vávra I.<sup>1</sup>,

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The nanoindentation technique was developed in the mid-1970s to measure the hardness of small volumes of material. We applied this technique for the study of mechanical properties of nanoporous molybdenum films prepared by magnetron sputtering at relatively high Ar pressure[1]. Nano-Hardness Tester NHT (CSM Instruments) was used for nanoindentation. Cross-sectional TEM specimen was prepared in Quanta 3Di instrument by Ga ion beam etching. The TEM analysis confirmed the plastic deformation of film and densification of Mo film in the immediate vicinity of the indent. The pores (observed in the starting specimen) disappeared. The load-displacement curves for nanoindentation test are interpreted by observed deformations in the indent region.

[1] Vávra, I., Križanová, Z., Dérer, J., Humlíček, J., : Vacuum 86 (2012) 742-744.



*Fig.1. Cross-sectional TEM of nano-indent region under the tip of nanoindenter. The plastic deformation of originally columnar porous nanostructure is clearly seen.*

Support by VEGA grant 2/0129/ and by APVV grant 0593-11 is acknowledged.

# Properties of metal nanoparticles prepared by pulsed laser ablation in ionic liquid

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Recently the synthesis of metal nanoparticles (NPs) in the ionic liquids (ILs) has been intensively studied due to the possibility of application of such complexes in electrochemistry and catalysis. Comparing to the polymeric stabilizing agents ILs possess such properties as intrinsic ionic charge, high polarity, high dielectric constant and supramolecular network that provide an electrostatic protective shell for metal NPs. Such electrostatic and coordination effects should facilitate the synthesis of the particles, protect them from aggregation and provide the mechanism of adjusting the properties of the NP-IL system.

Commonly metal NPs are synthesized by chemical (the reduction of organometallic compounds, decomposition of transition-metal complexes, or simple transfer of previously prepared colloids onto the ILs) and physical methods (vapor deposition onto ILs, and very recently, laser ablation). Laser ablation technique has advantages of eliminating chemical precursors, stabilizing agents and necessary further purification procedures. In this paper we used laser assisted techniques for production of gold and copper nanoparticles in 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>C<sub>1</sub>Im] [Tf<sub>2</sub>N], without the addition of any external chemical reagent. We used laser irradiation processes in several ways: first, laser ablation of the metal target immersed into IL, second, laser induced sputtering of the preliminarily prepared gold NPs placed under IL layer and finally additional laser irradiation of the NPs formed in IL with laser light at frequency of the surface plasmon resonance.

Laser ablation experiments were carried out using the radiation of a Nd:YAG laser (LOTIS TII, LS2134D), operating at 1064 nm (maximum pulse energy 80 mJ, repetition rate 10 Hz, pulse duration 8 ns). For laser-induced modification of nanoparticles the unfocused beam of the second harmonic (wavelength 532 nm) of the same Nd:YAG laser was used. The maximal laser irradiation fluence was 0.3 J/cm<sup>2</sup>. The optical properties, morphology and size distributions of the synthesized nanoparticles were investigated using UV/VIS absorption spectroscopy and transmission electron microscopy (TEM).

Optical absorption spectra of the synthesized gold colloids exhibited the characteristic peaks of the surface plasmon resonance (SPR) on the tail of the broad band extending toward the UV-wavelength range and originating from the interband transitions in nanoparticles. The plasmon peak position was around 545–560 nm for gold and 590 nm for copper indicating the formation of particles with dimensions of 5–20 nm. The plasmon peak positions were found to be sensitive to the additional laser irradiation. The blue shift of the SPR maximum and narrowing of the red tail of the plasmon resonance band after 532 nm irradiation can be attributed to the depletion of the particle aggregates and fragmentation of parent nanoparticles into smaller ones after the additional laser irradiation. These spectra findings were confirmed by TEM data.

This work was partially financed by the APVV grant number 0593-11 and by the Belarusian Foundation for Fundamental Researches under Grant No. F 12OB-020.

## Biodistribution of Paclitaxel in the form of magnetic nanospheres

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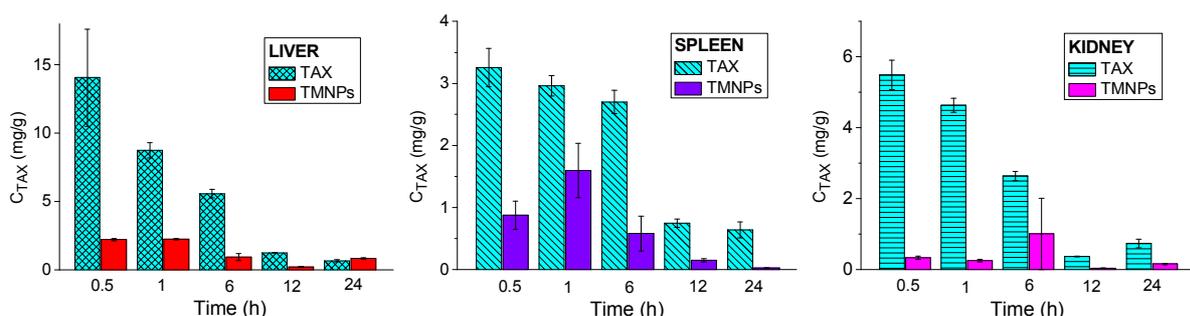
<sup>1</sup>*Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Kosice, Slovakia*

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The aim of this work was to study the time dependence distribution of anticancer drug Paclitaxel (Taxol, TAX) applied in the form of magnetic nanospheres (NPs) and to examine tumour reduction in comparison with non-targeted delivery. Paclitaxel loaded magnetic NPs were prepared and tested *in vivo* in mice. The polymer matrix for the encapsulation of the drug and magnetic Fe<sub>3</sub>O<sub>4</sub> particles was created by poly(lactide *co* glycolide) (PLGA).

Paclitaxel loaded in magnetic NPs at applied an external field had a different biodistribution than paclitaxel administered in Cremophor based injection formulation (Fig. 1). Biodistribution of TAX was determined in the plasma, selected organs (liver, lung, spleen, kidney, heart) and the target tissue (placed in magnet pole during the treatment). The organ of the highest TAX content after i.v. administration of its injection form was the liver. The following organs of high affinity were the spleen and the kidney.

For studying of tumour treatment efficiency several compositions of NPs with different magnetite/drug ratio were tested. The drug loaded magnetically targeted NPs caused a reduction of tumour weight. The therapeutic effect at four doses of 5 mg/kg in tumour bearing mice C 57BL/6 (B16 melanoma) kept in magnetic field for 30 minutes after intravenous administration was comparable with the effect of injection paclitaxel formulation. A better result was achieved using the composition with higher magnetite/drug weight ratio than in the sample with the smaller ratio what is due to fact that the samples with higher magnetite content were trapped more effectively in the target site (tumour) by the external field. The tumour was destroyed in both cases.



**Fig. 1** Biodistribution of TAX in selected organs (content in one gram) as a function of time after i.v. administration. Comparison of TAX injection formulation (with Cremophor) and of TMNPs (TAX:PLGA:Fe<sub>3</sub>O<sub>4</sub> 10:100:50) using an external magnetic field for 30 min.

### Acknowledgment

This work was supported within the projects 26220220005, 26110230061 and 2622012033 in the framework of the SF of EU, CEX of SAS Nanofluid, VEGA 2/0041/12, 0077, 2/0051/09, APVV 99-026505, 0742-10 and 0171-10.

## **Monophase Fe<sub>23</sub>B<sub>6</sub>-type alloy formed by crystallization of rapidly quenched Fe-Ni-Nb-B system**

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The study is focused on rapidly quenched amorphous Fe-Ni-Nb-B system in a wide compositional range of substitution of Fe by Ni with varying boron content. This system is known to have a good glass forming ability and to crystallize in either two distinct transformation stages or in one single step, depending on the boron content and on the ratio of Fe to Ni. On the basis of our results we have identified and quantified the formation of a complex phase (Fe-Ni-Nb)<sub>23</sub>B<sub>6</sub> alongside with fcc-FeNi. In a specific case it was possible to obtain only a single-phase Fe<sub>23</sub>B<sub>6</sub> type alloy and thus to explore and characterize this phase, especially as there is no prior evidence of preparing such a monophase system. Detailed characterization of composition, structure and selected magnetic properties of both phases is presented. We have proposed a model of possible local structural and chemical arrangement in (Fe-Ni-Nb)<sub>23</sub>B<sub>6</sub> phase as well as possible building units responsible for specific features of transformation from amorphous state and for preferential formation of this phase. This was confirmed by refinement of selected X-ray patterns together with high resolution (S)TEM analysis combined with energy filtered TEM. EFTEM analysis has shown a unique interface between the Fe<sub>23</sub>B<sub>6</sub>-type phase and the remaining FeNi matrix in systems where both phases were present. On the other hand, high resolution z-contrast STEM analysis applied to a single phase system revealed atomic positions of constituent atoms. Niobium was confirmed on positions as predicted by the proposed structural model and as refined from the diffraction experiments. Conventional high resolution TEM analysis was used to characterize the Fe<sub>23</sub>B<sub>6</sub>-type grains with respect to defects and faults.

## Nanocrystalline phase elaborated by thermally activated crystallization of amorphous Fe–Sn–B ribbons.

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<sup>2</sup>Vlastimil Vodárek

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Fe–B based amorphous alloys representing a classical metallic glass system with interesting soft magnetic characteristics have been widely inspected in hundreds of scientific papers [1,2]. Significant contribution was the discovery of formation of nanocrystalline phase by controlled crystallization of Fe–B based amorphous alloys containing small addition of specific elements, e.g. Cu, Nb [3]. Recently also nanocrystallization has been referred for the Fe–B based ribbons as the consequence of extreme heat-treatment [4].

In this study the crystallization of the Fe–Sn–B amorphous ribbons (prepared by planar-flow casting) is explored in details. Its kinetics was characterized by differential scanning calorimetry using Perkin-Elmer DSC7. The microstructure and morphology of the crystallized products was analyzed by transmission electron microscopy using conventional JEOL 2000 FX and high-resolution JEOL JEM-2100 (LaB<sub>6</sub>) microscopes and standard X-ray diffraction using CuK $\alpha$  radiation. Namely hypocritical composition Fe<sub>78</sub>Sn<sub>5</sub>B<sub>17</sub> was chosen exhibiting two distinct crystallization steps controlled mainly by classical nucleation-and-growth (JMA) kinetics as determined by DSC [5].

Microstructural study of the first step reveals formation of specific nanocrystalline phase consisting of grains of bcc-Fe(Sn) with equiaxed morphology and size up to ~50nm, which are of rather high population embedded in remaining amorphous matrix. High-resolution analysis shows their rather faulted inner structure which should be a consequence of incorporation of Sn atoms into Fe crystalline lattice (no clustering of Sn atoms was observed). This phase remains present up to higher stage of second crystallization step which corresponds to transformation of remaining amorphous matrix to iron borides via rather complex process. It starts by formation of larger spherulitic grains of metastable iron borides (mainly tetragonal Fe<sub>3</sub>B detected), which are then transformed to smaller polyhedral grains of stable Fe<sub>2</sub>B. This transformation involves decrease of supersaturation of Fe(Sn) with Sn accompanied by formation of hexagonal FeSn.

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# **Structure and Kinetics of Metastable Systems based on Fe-Co-B-Si-(P)- (Cu)**

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Metastable systems based on Fe-Co-B-Si with additions of P and Cu exhibit high saturation induction and high permeability. The samples were prepared by rapid quenching (planar flow casting) in form of 6 mm wide thin ribbons. Physical properties of these materials are dependent on the occurring crystalline phases transforming from amorphous state after the controlled heat treatment. The changes of the obtained metastable phase, the crystallization process, were investigated by differential scanning calorimetry (DSC). The phases were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The crystallization kinetics and the corresponding activation energies were determined using the Kissinger dependence. The Curie temperature of the ferromagnetic transition has been determined by the TGA measurements. Mechanical properties were obtained from relative stress measurements at break. The effect of the substitutions of the additions on structure in nanocrystalline state was investigated.

## **On the structure evolution in q-phase rapidly solidified Al<sub>65</sub>Fe<sub>15</sub>Si<sub>20</sub> composite**

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Recently a possible new highly ordered non-crystalline phase in rapidly solidified Al<sub>65</sub>Fe<sub>15</sub>Si<sub>20</sub> was reported.(1). To confirm this observation the Al<sub>65</sub>Fe<sub>15</sub>Si<sub>20</sub> alloy was rapidly quenched from the melt (planar-flow casting technique) into a shape of a very brittle thin ribbon. The phase composition of the sample was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) in as-cast as well as during and after heat treatment. Possible magnetic properties were checked by TGA measurements. The evolution of a phase structure and the crystallization process were investigated by differential scanning calorimetry (DSC). The observed preliminary results are discussed.

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## List of Authors

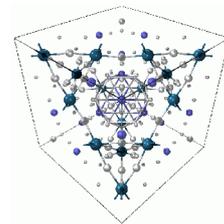
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Balog, M.	O-2	Kašiarová, M.	<b>O-20</b>
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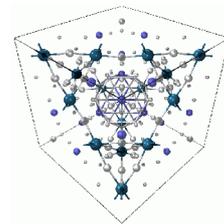
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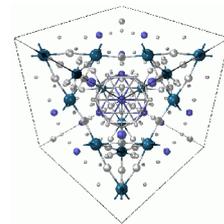
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