The basic research in the Department for Nanostructured Materials focuses on inorganic materials whose specific physical properties are a consequence of their structural and chemical characteristics at the nanometer and atomic levels. The research involves natural and manufactured ceramic materials as well as metals and intermetallic compounds. The objective is to find relationships between the physical properties of a material and its structural and chemical properties, using electron microscopy techniques to reveal phenomena on the nanoscale. Macroscopic phenomena, for example, phase transformations, phase equilibria, polytypism, polymorphism, crystal growth and the development of the microstructure are all areas of particular interest.

Research in the field of intermetallic alloys was continued in two main areas; Sm-Fe-N and Nd-Fe-B based permanent magnets. The magnetic behavior of Sm$_{13.7}$Fe$_{86.3}$ and Sm$_{13.8}$Fe$_{82.2}$Ta$_{4.0}$ materials during the hydrogenation-disproportionation-desorption-recombination (HDDR) and subsequent nitriding processes was investigated using a specially designed vibrating-sample magnetometer (VSM) modified with a high-temperature (up to 1000°C) vacuum-gas system. The techniques rely on detecting the moment of the ferromagnetic iron as it is formed during the disproportionation process. This method has the advantage of detecting the main product of the disproportionation reaction directly, rather than relying on secondary effects such as a drop in pressure or a change in resistance.

The results show that the initial absorption of hydrogen results in an increase in magnetization as well as in Tc, and that the sluggish disproportionation of the Sm$_2$Fe$_{17}$ phase in the Sm$_{13.8}$Fe$_{82.2}$Ta$_{4.0}$ sample is due to dissolved Ta. Monitoring the nitriding process shows that the magnetization increases as the sample picks up nitrogen at around 250°C. If the sample was previously HDDR-ed, the nitrogen uptake goes very smoothly whereas, if the samples are not HDDR processed, the nitrogen reaction also involves decomposition of the SmFe$_5$ and SmFe$_7$ phases. The disproportionation reaction for Nd-Fe-B type materials was investigated using our modified vibrating-sample magnetometer. Our investigations of Pr-substituted, Zr-doped Nd-Fe-B-based materials have led to the identification of a two-stage disproportionation reaction in Zr-free materials at temperatures in the range 600–650°C. These results suggest that the standard Johnson–Mehl–Arravis–Kolmogorov (JMAK) model is inadequate for describing the process of disproportionation in these alloys, and that an extension to the JMAK theory that takes into account a critical radius for stable iron nuclei is required to explain these low values.

The evolution of microstructure during the HDDR preparation of hard magnetic powders for bonded magnets, based on Nd-Fe-Dy-B as the basic material, was studied using the transmission electron microscopy. The distribution of phases, grain size and morphology of NdH$_2$, Fe$_2$B and α-Fe in samples prepared under various conditions were investigated. It was found that certain crystallographic relationships exist between several phases, which could explain the high degree of anisotropy of the final material. The result of the applied research in the frame of a NATO SfP was the pilot production of injection moulded bonded magnets.

We investigated nonlinear magneto-elastic coupling in 3d transition-metal epitaxial films by applying a phenomenological theory and by calculating the electronic structure. We calculated the X-ray-magnetic-circular-dichroism (XMCD) spectra, tested the corresponding sum rules and studied the influence of the magnetic dipolar term. We investigated the magnetic properties (XMCD, magnetic moments and magnetic anisotropy) in nanowires, within the framework of the density functional theory.

In numerous ceramic materials with perovskite and wurtzite structure we demonstrated the influence of planar faults and polytypic sequences on exaggerated grain growth, which can be beneficially exploited for microstructure tailoring. We optimised the composition of varistor blocks used for high voltage arresters. In the field of electron microscopy we implemented Z-contrast imaging (HAADF-STEM), which enables quantitative chemical analysis of individual atomic columns based on differences in their intensities.
The nucleation and crystallisation of calcium carbonate in tap water under the influence of a magnetic field is the subject of continuing studies. Using analytical electron microscopy it was found that the nucleation of all three crystal phases is much slower under the magnetic field. The ratio of calcite, aragonite and vaterite crystal forms is also strongly influenced by the presence of the field.

In materials used as optical elements in laser nanolithography, such as various fluorides doped with rare earths, the degree of chemical homogeneity was determined using energy dispersive X-ray spectroscopy. It was found that, in the range of a few nanometers, some inhomogeneous areas exist which influence the optical properties. The presence of nanometer sized clusters with different composition was investigated with STEM/ HAADF (Z-contrast). For the TEM study of the surface of silicone wafers covered with photoresist and irradiated with high-energy laser radiation we optimized the preparation of carbon replicas.

The research program of the group for electron microscopy was primarily focused on determining the structure and chemical composition of planar faults and polytypic sequences in various polycrystalline ceramic materials, using different electron microscopy techniques. The investigations of the phenomenon of exaggerated grain growth have led us to a systematic study of grain growth in ceramic materials with perovskite and wurtzite structures. Atomic resolution transmission electron microscopy showed, that as a rule, the exaggerated grains contain polytypic faults which can either be isolated or form ordered polytypic sequences. Faults of this type can only be observed in systems where a secondary polytypic phase with 3m symmetry. These results led us to systematic investigation of microstructure developments in ZnO doped with extremely small concentration of Sb+3, from 0 to a few 100s of ppm. We found that even very small amounts of Sb+3 caused the formation of inversion boundaries that determine further ZnO microstructure development. In ZnO-based varistor materials, doped with rare earth oxides (REO), we have studied the influence of Sb2O3 and Bi2O3/Sb2O3 ratio on microstructure and electrical properties of ZnO ceramics doped with Y2O3.

Applied research for Varsi d.o.o. continued with the development of varistor blocks for high voltage arresters for voltages up to 12 kV. By optimizing the starting composition, the binder burnout process and the sintering regime, we have achieved better final electric properties of the material. We have further collaborated with Varsi d.o.o. in developing energy varistors with different nominal voltages and shapes, for miniaturized and integrated modules for overvoltage protection. We are involved with Bosch in developing a Sr(Ti,Fe)O3 oxygen sensor.

In 2002 the group for electron microscopy carried out electron microscopy analyses of inorganic and organic materials for the following customers: Jožef Stefan Institute (K5, K9, F5, F3, K3), National Institute of Chemistry, Faculty of Pharmacy, Faculty for Natural Sciences, Faculty for Mathematics and Physics, Biotechnical Faculty, Slovenian Health Society, Pulp and Paper Institute, Slovenian Restoration Centre, Lek d.d., Krka, DONIT TESNIT d.d., BIA Separations d.o.o., Swaty d.d., Premogovnik Velenje d.d., EMO Kemija, Cinkarna Celje, IRMA, KEKO OPREMA, ERICO Velenje, and EKOM.

Some outstanding publications in the year 2002

BIBLIOGRAPHY

ORIGINAL ARTICLES

1. M. Algueró, Goran Dražić, Marija Kosec, M. L. Calzada, L. Parlo
   Evolucion microestructural durante la transformacion de la estructura picroclore en perovskita en lamillas de (PbLa)TiO3

2. A. Belloni, O. Gutfliehs, K.-H. Müller, L. Schultz, Goran Dražić
   High-performance nanocristaline PbF4-based magnets produced by intensive milling

3. A. C. Cefalas, Spomenka Kobe, Z. Kollia, E. Sarantopoulou
   Crystal field splitting of highly excited electronic states of the 4f5 5d electronic configuration of trivalent rare earth ions in wide band gap crystals

   Macrostructure imaging of biological specimens in vivo with laser plasma X-ray contact microscopy

5. Goran Dražić, E. Sarantopoulou, Spomenka Kobe, Z. Kollia, A. C. Cefalas
   X-ray microanalysis of optical materials for 157nm photolithography

6. Claude Ededer, Matej Komej, Manfred Fähnle, Gisela Schulz
   Theory of induced magnetic moments and x-ray magnetic circular dichroism in CoPt multilayers

7. M. Fähnle, Matej Komej, R. Q. Wu, G. W. Guo
   Magnetoelectricity of Fe: possible failure of ab initio electron theory with the local-spin-density approximation and with the generalized-gradient approximation

8. Manfred Fähnle, Matej Komej
   Second-order magnetoelastic effects: from the Dirac equation to the magnetic properties of ultrathin epitaxial films for magnetic thin-film applications

9. Marko Hrovat, Zoran Samardžija, Janez Holc, Darko Belavič
   The development of microstructural and electrical characteristics in some thick-film resistors during firing

10. Goran Dražić, E. Sarantopoulou, Spomenka Kobe, Z. Kollia, A. C. Cefalas
   Mechanism of the oxidation of the Fe-C-Si-Al-Zr alloys

11. Matej Komej, Claude Ededer, James W. Davenport, Manfred Fähnle
   From the bulk to monatomic wires: an ab initio study of magnetism in Co systems with various dimensionality

12. Matej Komej, M. Fähnle
   On the magnetic contribution to the magnetic anisotropy of thin epitaxial permalloy films: an ab initio study. letter to the editor

13. Matej Komej, M. Fähnle
   Shear-strain-related nonlinear magnetoelastic properties of epitaxial films

14. Matej Komej, M. Fähnle
   Determination of the complete set of second-order magnetoelastic coupling constants on epitaxial films

15. Miro Mandeljc, Barbara Mail, Marija Kosec, Goran Dražić
   Crystalization of zirconium-rich PLZT thin films below 500 °C

16. Paul J. McGuinness, Kristina Žužek, Goran Dražić
   Hydrogen absorption and desorption in Ta-doped SmFe-based alloys

17. Paul J. McGuinness, Kristina Žužek, Goran Dražić
   Analytical electron microscopy study of silver contaminated with various dimensionality

18. Manica Tonković-Prijanović, Ladislav Kosec, Jakob Lamut, Vasilij Gontarev, Zoran Samardžija
   Mechanism of the oxidation of the Fe-C-Si-Al-Zr alloys
   In: Metalurgija (Slo), Vol. 43, No. 1, pp. 17-22, 2002.

19. Kristina Žužek, Goran Dražić, Paul J. McGuinness, Goran Dražić
   Hydrogen absorption and desorption in Ta-doped SmFe-based alloys

MONOGRAPH

1. Angela Surca Vuk, Boris Orel, Goran Dražić, Philippe Colomban
   Vibration spectroscopy and analytical electron microscopy studies of Fe-V-O and In-V-O thin films

2. Angela Surca Vuk, Boris Orel, Goran Dražić, Jean-Claude Pons, Philippe Colomban
   UV-visible and IR spectroelectrochemical studies of FeVO4 sol-gel films for electrochromic applications

3. Kristina Žužek, Goran Dražić, Paul J. McGuinness, Goran Dražić
   Hydrogen absorption and desorption in Ta-doped SmFe-based alloys

PUBLISHED CONFERENCE PAPERS

Published Invited Conference Papers

1. Matej Komej, M. Fähnle
   Ab-initio study of the influence of epitaxial strain on magnetoelastic properties

2. Paul J. McGuinness, Spomenka Kobe
   Developing bonded HDP magnets for a Slovenian SME
1. Andrea Benčan, Marko Hrovat, Janez Holc, Goran Dražić, Marija Kosec
  Structural and electrical characterization of PZT films fired on nickel substrates

2. Slavko Bernalski, Aljoša Tavčar, Srečo Mašek, Mitja Hariš, Mitrajm Cergoš
  The development of miniaturized ZnO-based metal-semiconductor field-effect transistors


4. Goran Dražić, Sergej Zupan, Spomenka Kobe, Paul J. McGuinness
  VUV spectroscopy of nominally pure and rare-earth ions doped LiCaAlF6

5. Miran Čeh, Sašo Šturm, Aleksander Rečnik, T. Yamazaki, K. Watanabe, M. Shiojiri
  The influence of focus on resolution and contrast variations in experimental HAADF-STEM images

6. Nina Daneu, Thomas Walter, Aleksander Rečnik
  Test of a new analytical method to measure the composition of a planar fault in AOD-doped SrTiO3

7. Goran Dražić, Paul J. McGuinness
  Deconvolution process of high-resolution HAADF-STEM images

8. Goran Dražić, Sergej Zupan, Spomenka Kobe, Paul J. McGuinness, Janez Štržšar
  Stresses in high magnetic fields on calcium carbonate nucleation and crystallisation

9. Marko Hrovat, Darko Belavič, Andreja Benčan, Janez Holc, Goran Dražić
  XRD and microstructural characterization of 1 kohm/sq. thick-film PTC resistors
  In: Conference proceedings: Quality management and diagnostics in electronic processing of HAADS-STEM images

10. Goran Dražić, Paul J. McGuinness
  Distribution of oxygen in HDDR processed Nd-Dy-Dy-Co-B magnetic powders


13. N. Nakanishi, T. Yamazaki, Aleksander Rečnik, Miran Čeh, K. Watanabe, M. Shiojiri
  AEM study of the influence of focus on resolution and contrast variations in experimental HAADF-STEM images


19. N. Nakanishi, T. Yamazaki, Aleksander Rečnik, Miran Čeh, K. Watanabe, M. Shiojiri
  Deconvolution process of high-resolution HAADF-STEM images

20. T. Walther, Aleksander Rečnik, Nina Daneu
  The magnetic moment of trivalent rare-earth ions in ionic laser crystals

21. T. Yamazaki, Aleksander Rečnik, Miran Čeh, K. Watanabe, M. Shiojiri
  The influence of polytypic faulting on exaggerated growth of crystals: invited talk

22. T. Yamazaki, Aleksander Rečnik, Miran Čeh, K. Watanabe, M. Shiojiri
  On the structure and chemistry of twin boundaries in sphalerite crystals from Trepča mines in Kosovo

23. T. Yamazaki, Aleksander Rečnik, M. Kawasaki, Miran Čeh, K. Watanabe, M. Shiojiri
  A HAADF-STEM investigation of inversion boundaries in SnO2-doped ZnO ceramics

LECTURES - GUEST LECTURES AT FOREIGN UNIVERSITIES

1. Miran Čeh
  High-resolution HAADF STEM imaging of (Ca,Sr,Ba)TiO3 perovskites: invited talk
  Graz, Forschungsinstitut für Elektronenmikroskopie und Feinstrukturforschung, 10 Jan. 2002.

2. Miran Čeh
  Microscopic investigation of AO (A=Ca,Ca) b-doped perovskite: invited talk
  Shanghai, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 6 Dec. 2002.

3. Nina Daneu
  Grain growth control in SnO2-doped ZnO: invited talk

4. Aleksander Rečnik
  The influence of polycrystalline faulting on exaggerated growth of crystals: invited talk

5. Aleksander Rečnik
  Solving the atomic structure of inversion boundaries in Sn-doped ZnO: invited talk

6. Aleksander Rečnik
  Solving the atomic structure of inversion boundaries in Sn-doped ZnO: invited talk
  Oxford, Oxford University, Department of Materials, 1 Aug. 2002.
8. Resistive Exhaust Gas Sensors on the Basis of Temperature-independent Semiconducting Oxides; Electron Microscopy Investigations of SrTiO$_3$-Based Perovskites  
Dr. Wolfgang Mennesklou, Universität Karlsruhe, Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruhe, Germany  
Dr. Miran Čeh

9. Zinc Oxide Based Varistor Ceramics  
SVN 99/021  
Prof. Werner Mader, Universität Bonn, Institut für Anorganische Chemie, Bonn, Germany  
Dr. Aleksander Rečnik

10. Bonded Magnets Based on RE-TM Nanocrystalline Powders  
SVN 99/020  
Dr. K.-H. Müller, Dr. Oliver Gutfleisch, IFW Dresden, Institut für Festkörper und Werkstofforschung, Dresden, Germany  
Asst. Prof. Spomenka Kobe  
Dr. Paul McGuiness

11. Interfaces in Ceramics  
SVN 99/026  
Prof. Manfred Rühle, Max-Planck-Institut für Metallforschung, Stuttgart, Germany  
Dr. Miran Čeh

12. Cohesive Powder Fluidization Via Magnetic Excitation  
SLO-US 2001/36  
Prof. James F. Klausner, University of Florida, Gainesville, Florida, USA  
Asst. Prof. Spomenka Kobe

SLO-US 2001/49  
Dr. Ryna Marinenko, National Institute of Standards and Technology (NIST), Surface and Microanalysis Science Division, Gaithersburg, MD, USA  
Dr. Slavko Bernik

NEW CONTRACTS SIGNED

1. Varistors for miniaturised and integrated search protection devices  
VARSi d.o.o. Ljubljana  
Dr. Slavko Bernik

2. VARESTER: Miniaturised high-voltage arrester  
VARSi d.o.o. Ljubljana  
Dr. Slavko Bernik

3. MICROPROTEIN: Micrometer Scale Patterning of Protein and DNA Chips  
National Hellenic Research Foundation - NHRF, Theoretical and Physical Chemistry Institute, Athens, Greece  
Asst. Prof. Spomenka Kobe, Dr. Goran Dražič

4. Resistive Exhaust Gas Sensors on the Basis of Temperature-independent Semiconducting Oxides  
Universität Karlsruhe, Institut für Werkstoffe der Elektrotechnik - IWE, Karlsruhe, Germany Dr. Miran Čeh

5. Morphology studies of active substances and pharmaceutical products  
Lek d.d. Ljubljana  
Dr. Miran Čeh

VISITORS FROM ABROAD

1. Dr. Oliver Gutfleisch, Institut für Festkörper und Werkstofforschung – IFW, Dresden, Germany, January 24 - 27, 2002

2. Rahmati Behnaz, B.Sc., Max-Planck-Institut für Metallforschung, Stuttgart, Germany, January 26 - February 1, 2002

3. Prof. Bui Ai, Université Paul Sabatier, Laboratoire de Génie Électrique, de l’Électricité, Toulouse Cedex, France  
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4. Prof. Constantinos Cefalas, National Hellenic Research Foundation - NHRF, Theoretical and Physical Chemistry Institute, Athens, Greece, April 27 - May 1, 2002

5. Dr. Ryna B. Marinenko, National Institute for Standards and Technology - NIST, Surface and Microanalysis Science Division, Gaithersburg, Maryland, USA, September 6 - 14, 2002

6. Prof. Makoto Shiojiri and Prof. Saijo Hiroshi, Kyoto Institute of Technology, Kyoto, Japan, September 27 - October 4, 2002

7. Takashi Yamazaki, B.Sc., Tokyo University of Science, Tokyo, Japan, September 28 - October 4, 2002


10. Prof. Constantinos Cefalas, National Hellenic Research Foundation – NHRF, Theoretical and Physical Chemistry Institute, Athens, Greece, October 21 - 25, 2002

11. Elena Tchernychova, B.Sc., Max-Planck-Institut für Metallforschung, Stuttgart, Germany, November 17 - 30, 2002
12. Prof. Wayne D. Kaplan, Technion – Israel Institute of Technology, Department of Materials Engineering, Haifa, Israel, December 1 - 8, 2002
13. Amir Avishai, B.Sc., Technion – Israel Institute of Technology, Department of Materials Engineering, Haifa, Israel, December 1 - 14, 2002
14. Yaron Kaufmann, B.Sc., Technion - Israel Institute of Technology, Department of Materials Engineering, Haifa, Israel, December 1 - 22, 2002

ORGANIZATION OF CONFERENCES AND MEETINGS

1. 17th International Workshop on Rare Earth Magnets and Their Applications, 12th Symposium on Magnetic Anisotropy and Coercivity in RE-TM Alloys, August 18 - 22, 2002, Newark, Delaware, USA (membership in International Advisory Committee)
2. 15th International Congress on Electron Microscopy, ICEM 15, Durban, South Africa, September 1 - 6, 2002 (co-organization)
3. 10th Conference on Materials and Technologies, Portorož, Slovenia, November 13 - 15, 2002 (co-organization)

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