RUHR-UNIVERSITÄT BOCHUM

RUB

Materials Research Department

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news

Research Insights and Information

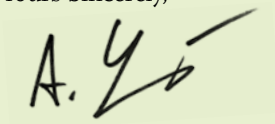
Editorial

DEAR READER,

This newsletter provides information about current research projects which are pursued by members of the Materials Research Department (MRD). These projects deal with high temperature steels, gas-metal interactions at high temperatures, thermoelectric materials, ferromagnetic shape memory materials, as well as ionic liquids in materials chemistry. Furthermore, a summary of highlights from the project SFB 491 "Magnetic Heterostructures", which is in its final phase, is presented. Moreover, the materials science related work of RUBION, a central facility of RUB, is reported.

An information for our German-speaking readers: a special issue of RUBIN (RUB's research magazine) on Materials Engineering was published recently. It can be purchased at the Institute of Materials or downloaded at http://www.rub.de/rubin/werkstoffe/beitraege/beitrag13.html.

Yours Sincerely,



Prof. Dr.-Ing. Alfred Ludwig

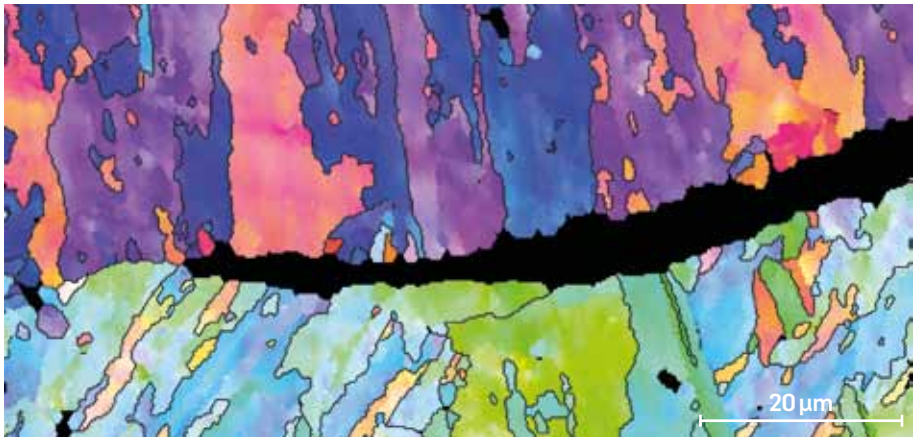


Figure 1: Crack tip area in a steel exhibiting brittle fracture. Note that the crack is sharp and intergranular, in contrast to the sample above.

Investigating failure mechanisms in high-temperature steels

Environmental, economic and geopolitical concerns about energy usage have come into prominence more and more in recent years. One approach to tackling these problems is the development of clean, renewable energy sources such as solar and wind generation. A complementary approach, especially in the short term, is to improve the efficiency of existing technologies, including fossil-fired power plant, so as to reduce the fuel consumption and greenhouse gas emission per unit of power generated. Efficiencies can be increased by raising the temperature and pressure of the steam, but the maximum steam conditions are limited by the high-temperature mechanical strength of the steam turbine rotors. These rotors, as well as the boilers and pipes transporting steam and superheated water, are often fabricated from a class of material known as tempered martensite ferritic steels (TMFS), which have a fine and complex microstructure consisting of a high density of dislocations, grain and subgrain boundaries and fine precipitates, all of which contribute to the resistance of the microstructure to thermally induced plastic deformation (creep). However, long-term exposure to high temperatures and pressures leads to a degradation of the microstructure and a reduction in its creep resistance. In order to ensure safe operation and avoid component failure, we need a comprehensive understanding of the relationship between microstructure and mechanical behaviour, and how this evolves over time at high temperature. One of the main ways in which data on creep properties and their relationship with microstructure are obtained is by performing tests on standardised specimens under different conditions of temperature and applied stress. The tests can either be continued until failure or interrupted to examine the microstructure at intermediate stages.

The microstructure of TMFS has important features on multiple length scales and complementary techniques are used to obtain a comprehensive characterisation. Transmission electron microscopy (TEM) is used to study the sizes of subgrains and precipitates, and energy dispersive X-ray spectroscopy (EDX) to determine the compositions of the precipitates. Dislocation densities can be determined using TEM and X-ray diffraction. Another technique, which has become more widespread in the past few years, is the use of electron backscatter diffraction (EBSD) in the scanning electron microscope for characterisation, on the scale of several tens to several hundreds

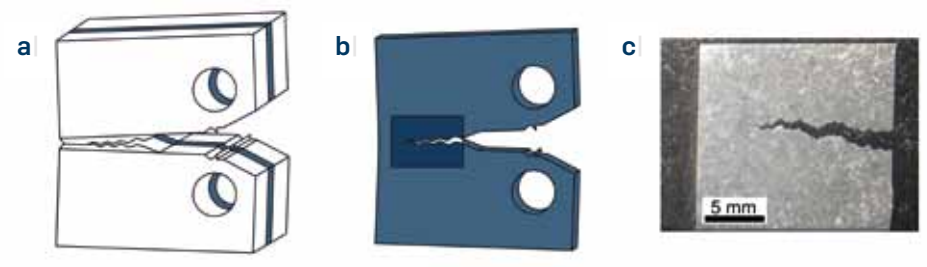


Figure 2: Preparation of a cracked specimen for EBSD: (a) a crack growth test is interrupted part-way through and a thin vertical section (blue) is cut out of the specimen; (b) the area around the crack is cut out; (c) a metallographic specimen polished for EBSD – a strain-free surface is essential so careful polishing is important

of microns, of the crystallographic orientations of grains and subgrains. This enables us to see easily whether grains and subgrains are growing, whether recovery (reorganisation of dislocations into grain boundaries) and recrystallisation (formation of new grains with low dislocation density) are occurring, or whether grains are being rotated into new directions under the action of the applied stress. Figure 2 shows how an EBSD specimen is prepared from a standard crack growth test specimen.

EBSD analysis, coupled with the other techniques, can give insight into the types of microstructural site that most favour nucleation and propagation of voids and cracks, as well as the effect of stress, high temperature and the presence of voids and cracks on the microstructure locally. Figure 3 is an example from an interrupted crack growth test specimen of a steel used for power-plant boilers and pipes. This material is relatively resistant to cracks, which form in a slow and ductile manner rather than by sudden, rapid propagation, which could be catastrophic in vessels containing high-pressure steam. The black regions represent voids formed during testing, and the different colours represent different crystal orientations. The wire-frame images also show the orientations of the crystallites. In the region between the two voids, where only a thin, highly stressed "bridge" is preventing the voids from joining together to form a larger crack, the stress has caused the subgrains to rotate locally from their original orientations into new ones. Steels that fail in a more rapid, brittle manner in crack growth tests do not show this type of rotation behaviour; instead, mainly sharp, straight cracks are found along grain boundaries with very little modification to the substructure within the grains (see Figure 1). We are therefore able to see a clear quantitative agreement between macroscopic cracking behaviour and the appearance of EBSD micrographs. We are currently working on using crystallographic parameters derived from EBSD data to obtain quantitative measures for local plastic deformation in the vicinity of cracks and voids. In parallel, we are investigating in more detail the grain rotation process, in the hope of obtaining a more fundamental understanding of how deformation occurs in these technologically important materials.

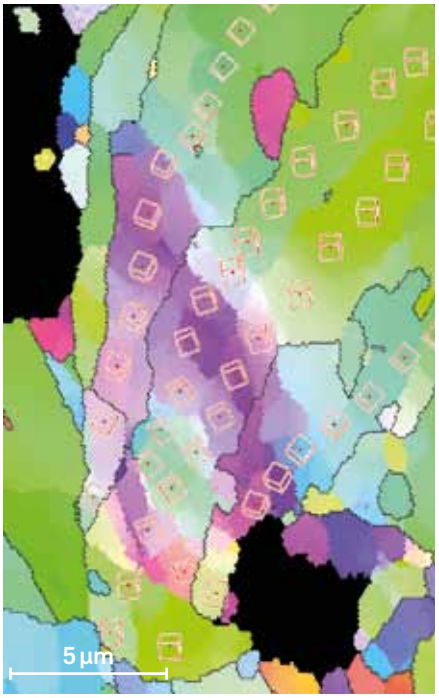


Figure 3: Localised changes in crystal orientation in a highly stressed region between two voids in a sample showing ductile fracture

Dr. Victoria Yardley
Juniorprofessor of Microstructure of Materials
Email: victoria.yardley@rub.de

Material analysis and modification by ion beams

The Central Unit for Ion beams and Radionuclides (RUBION) emerged from the fusion of two laboratories in order to provide, develop and maintain equipment for experiments in all fields of natural sciences. RUBION has a department specialized in handling radioactive isotopes primarily used in medicine and life sciences as well as a department that operates different types of ion accelerators used in geology, physics, chemistry and materials science. The accelerator facility has one of the best systems in Europe and therefore is used by a large number of both national and international partners. Ion beam accelerators can be used for material analysis to investigate the structure or composition of new materials or for material modification like ion implantation.

Ion Beam Analysis

Ion beam analysis (IBA) is based on the detection of particles or radiation from sample material produced by ion beam bombardment. The spectrum of this secondary emission contains information about the sample. Depending on the technique, the stoichiometry, thickness of layers or the depth profile of certain elements can be determined.

RUBION operates three accelerators covering a wide energy range of ion beams for a wide variety of ion species and offers several IBA techniques. Frequently performed

Figure 1: The 500kV single ended accelerator. RUBION operates ion facilities from 5kV table top system to a 4 MV tandem accelerator with up to 60 m beam lines.

methods are Rutherford backscattering (RBS), nuclear reaction analysis (NRA) and particle induced X-ray emission (PIXE).

Scientists of many faculties of the Ruhr-Universität Bochum and other institutions

from all over the world are using the services at RUBION to analyze their sample materials with regard to their special questions. Chemists doing research on thin films deposited by metal-organic chemical vapor deposition (MOCVD) need to characterize these films to determine their stoichiometry. Engineers working in the field of hydrogen storage in solids have their samples analyzed for their hydrogen concentration. Mineralogists studying diffusion in minerals obtain results in form of depth profiles showing the diffusion process. Researchers of material sciences working on coatings for nuclear waste disposal are provided with exact information about the coating composition achieved. There are many further research fields like environmental research, archeology or astrophysics, where the IBA techniques at RUBION provide essential support. Sometimes the results are achieved by a combination of methods or with additional information from further analytical methods.

Continuously, upgrades of IBA setups are developed. The technique of induced gamma-ray emission by deuterons is a special NRA methods to detect lighter elements like carbon, nitrogen or oxygen. It was established at RUBION and now complements RBS measurements, which are less sensitive to these light elements. A further development improves the hydrogen detection and increases its sensitivity. The setup was equipped with a sputter gun and a sample heating system for surface cleaning inside the NRA vacuum chamber. Additionally, the possibility for hydrogen and water loading was installed. This enabled us to obtain new results about the hydrogen concentration of ZnO crystals and their surface coverage recently.

Ion Beam Modification

Beside the facilities for analytic techniques the tandem accelerator at RUBION is equipped with several end stages for high and low energy implantation, both for research and industrial use.

Ion beam implantation is a very important step in the production of modern electronic devices. However, the kinetic ion energy that is applied drops from several hundred keV to a few hundred eV with decreasing structure size. Whereas high energy (10-20 MeV) ion beams are still common in the production of radioisotopes for medical drugs or analysis of wear measurements, industrial ion beam implantation using energies of several hundred keV to a few MeV becomes less frequent in industrial mass production. This is mainly due to both historical as well as technical reasons. For instance, the accelerators require a proper shielding for safety and therefore do not fit easily inside a clean room.

Nevertheless, we predict that this trend will be reversed and industrial implantation using ion beams of several MeV will gain more attention in the next years. The number of products, which require this kind of implantation, is growing and the technique becomes more efficient due to new developments. The potential applications range from the implantation of radioactive ions for cancer treatment to carrier life-time adjustment in modern power devices decreasing the electrical power consumption. With the ion accelerators at RUBION we show that the results of university research and industrial production can be combined fruitfully.

One major research topic in RUBION is the development of quantum systems: The coupling of electronic spins of nitrogen vacancies (NV) is a promising approach to develop a basic component for quantum computing. RUBION established a method to artificially create NV centers using microbeam implantation. It allows a controlled implantation of ions in a defined depth with high lateral precision. This method is applied to produce samples for a large number of research groups from all over the world. We have shown that implantation using a focused nitrogen beam enables one to create pairs of NV-centers with a distance of only a few nanometers. This development led to the first quantum mechanical coupling of NV centers at room temperature.

Further developments in ion implantation techniques enabled us to address single atoms with high lateral resolution. This requires a low energetic ion beam to avoid ion beam straggling. We developed a collimated nanosystem based on a pierced AFM-tip. The system allows implantation with a lateral resolution below 20 nm. An further improvement of a single ion implanted setup based on an ion trap. This project, in cooperation with a group from Mainz, potentially allows the implantation of countable single ions with a resolution within one nanometer.

Zentrale RUBION
Einrichtung für Ionenstrahlen und Radionuklide


Dr. Detlef Rogalla
RUBION
Email: rogalla@rubion.rub.de


Dr. Sébastien Pezzagna
RUBION
Email: sebastien.pezzagna@rub.de


Dr. Hans-Werner Becker
RUBION
Email: hans-werner.becker@rub.de


PD Dr. Jan Meijer
Business Manager RUBION
Email: jan.meijer@rub.de

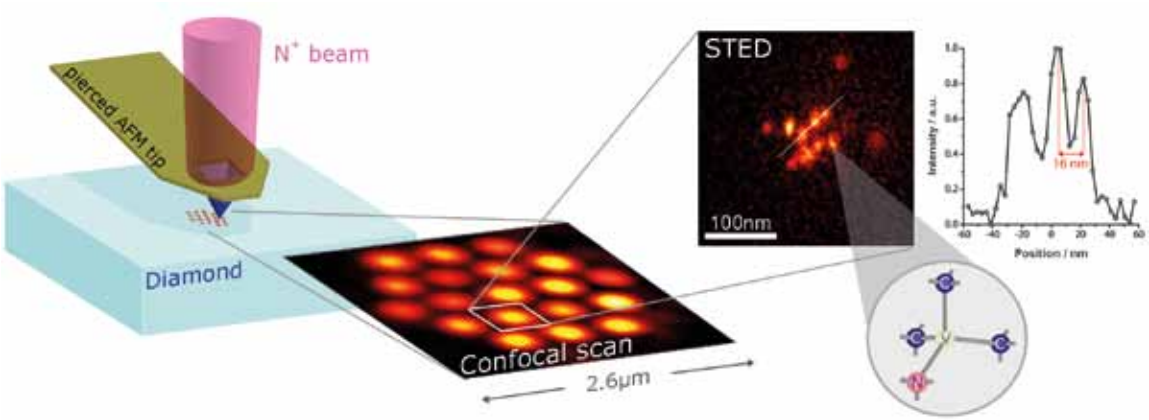
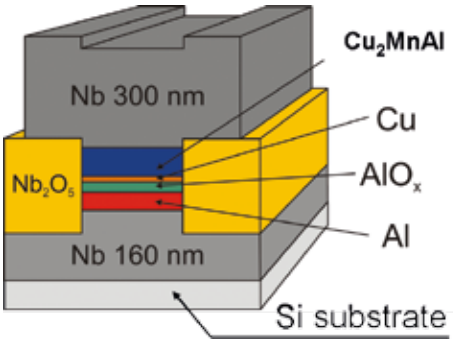


Figure 2: Nanoscale engineering and optical addressing of single NV centres in diamond. The implantation of low energy nitrogen ions is realised through the pierced hollow tip of the atomic force microscope. A STED scan of one particular spot reveals an ensemble of 12 single NV centres imaged with 10 nm resolution.

SFB 491 "Magnetic Heterostructures":

Twelve years of a successful research cooperation arrives at its conclusion



Design of a Josephson junction with a magnetic Heusler barrier (Cu_2MnAl) for showing the existence of triplet Cooper pairs.

'Magnetic Heterostructures: Spin Structures and Spin Transport' is the title of the collaborative research center SFB 491 that investigates physical principles of future information and communication technologies based on the spin of electrons in addition to their charge. The German Science Foundation (DFG) has funded this SFB for 12 years from January 2000 until December 2011 and has spent about 19 Million Euros, with additional funds from the State NRW. The research activity of the SFB 491 involved about 50 scientists in 19 different research groups located in the Departments of Physics and Electrical Engineering at the Ruhr-University Bochum and the University Duisburg-Essen. Chairperson of the SFB 491 was Prof. Dr. Dr. h.c. Hartmut Zabel (Ruhr-University Bochum), co-chair was Prof. Dr. Michael Farle (University Duisburg-Essen).

The research results are documented in more than 550 publications, 60 dissertations, several patents, and two review books on magnetic hetero- and nanostructure, one of which will appear in the spring of 2012. This scientific output has generated considerable attention and reputation for the SFB 491. Although the funding will end in December 2011, much more work remains to be done in the area of spintronics and is being perused by many groups worldwide.

From the numerous scientific highlights that were achieved during the term of the SFB 491, only a few which have particular relevance for materials science can be mentioned here. The field of spintronics and magneto-electronics requires special knowledge of ferromagnetic materials, semiconductors, superconductors, oxides, and their interfaces. For spin-related devices, such as spin valves, ferromagnetic materials are required that exhibit a very high spin polarization at the Fermi energy. **Heusler alloys** with the $L2_1$ structure are well known as half-metallic ferromagnets with a theoretically predicted 100% spin polarization for perfectly ordered superstructures. Although this full spin polarization has not been achieved yet in real spintronic devices, the very high tunnel magnetoresistance in magnetic tunneling junctions with Heusler alloy electrodes is highly promising for future device applications. Therefore thin film growth of Heusler alloys and optimization of their magnetic properties was pioneered within the SFB 491. In particular, the connection between structural order and magnetic moments in Heusler alloy films of only a few nanometer thickness, such as Co_2MnGe and Co_2MnSi were intensively investigated via x-ray and neutron scattering and by associated magnetometry. One remarkable result is the observation that local $L2_1$ order is sufficient in order to develop the full magnetic moments of Co and Mn.

Another area of considerable activity within the SFB 491 was the so called **exchange bias effect**. This effect refers to a shift of the ferromagnetic hysteresis with respect to the applied magnetic field, such that the coercivity for the descending branch and the ascending branch has different field values. This shift occurs when a ferromagnetic film is in contact with an antiferromagnetic substrate by a common interface, and after cooling the saturated ferromagnetic film below the Néel temperature of the antiferromagnet. The exchange bias effect is used in spin valves, which consist of two ferromagnetic films separated by a non-magnetic film. One ferromagnetic film is pinned via the exchange bias effect to the antiferromagnetic substrate, while the other ferromagnetic film can be freely rotated in an external magnetic field. Thus parallel and antiparallel orientations of both ferromagnetic films can be achieved, showing very different resistance values, which in turn can be used as magnetic field sensors, for instance in hard disks. While the basic principle of the exchange bias effect is well understood, the details of the ferromagnetic/antiferromagnetic interface were by no means clear. Detailed theoretical and experimental investigations of the interface properties showed that more insight into the exchange bias effect can be gained by assuming that there are domains in the antiferromagnet and that a certain amount of spin disorder exists at the ferromagnetic/antiferromagnetic interface. Furthermore the magnetic anisotropy of the antiferromagnet plays a crucial role. Is the antiferromagnet too soft, then the pinning of the ferromagnetic layer is ineffective.

One of the central themes of the SFB 491 was **proximity effects** between ferromagnets and superconductors. It is well known that bound pairs of electrons forming a singlet state (Cooper pairs) cannot penetrate far into ferromagnets. Rather, they will break up and each spin will line up individually with the magnetic field inside of the ferromagnet. Thus, if a superconducting film and a ferromagnetic film are in contact via a common interface, the superconducting transition temperature is rapidly suppressed. There are two ways to overcome this incompatibility between superconductors and ferromagnets. First the ferromagnetic film may develop a domain structure below the superconducting transition temperature. This is called a crypto-ferromagnetic state. Second, the Cooper pairs may arrange such that one electron spin lines up with the ferromagnet and the other electron with opposite

spin remains in the superconductor. Then, at the interface the superconductor is oppositely magnetized in relation to the ferromagnetic layer. This spin arrangement is termed the "inverse proximity" effect. Moreover, theorists in Bochum have predicted a new type of Cooper pair, which has a better chance of survival in ferromagnetic materials. In such Cooper pairs the electrons pair up in a triplet state. Triplet Cooper pairs are rare species. Nevertheless they can be filtered out of the superconducting condensate by using magnetic layers with a non-collinear spin structure, such as twisted ferromagnetic layers or spin glass materials which exhibit a certain amount of spin disorder. Experimental groups at the Ruhr-University together with a team at the National Research Center Jülich (FZJ) have teamed up to prove the existence of triplet Cooper pairs using a Josephson junction featuring a tunnel barrier sandwiched by two superconducting layers. The tunnel barrier consists of an oxide insulator, usually alumina. Tunneling of a large number of Cooper pairs results in a tunnel current, but if the barrier is thicker than a one or two nanometers, the tunnel current subsides. If the oxide tunnel barrier is replaced by a ferromagnetic layer, no Cooper pairs are able to pass through unless the magnetic barrier is twisted or disordered. The researchers have used Heusler alloys as the magnetic barrier, where the magnetic order can be fine tuned by annealing. With this barrier, tunnel currents could be detected that were much greater than expected for singlet Cooper pairs, providing evidence that the tunnel current was indeed supported by triplet Cooper pairs.

Prof. Dr. Dr. h.c. Hartmut Zabel
Professor of Solid State Physics
hartmut.zabel@ruhr-uni-bochum.de

Gas-solid interactions on metallic surfaces at high temperatures

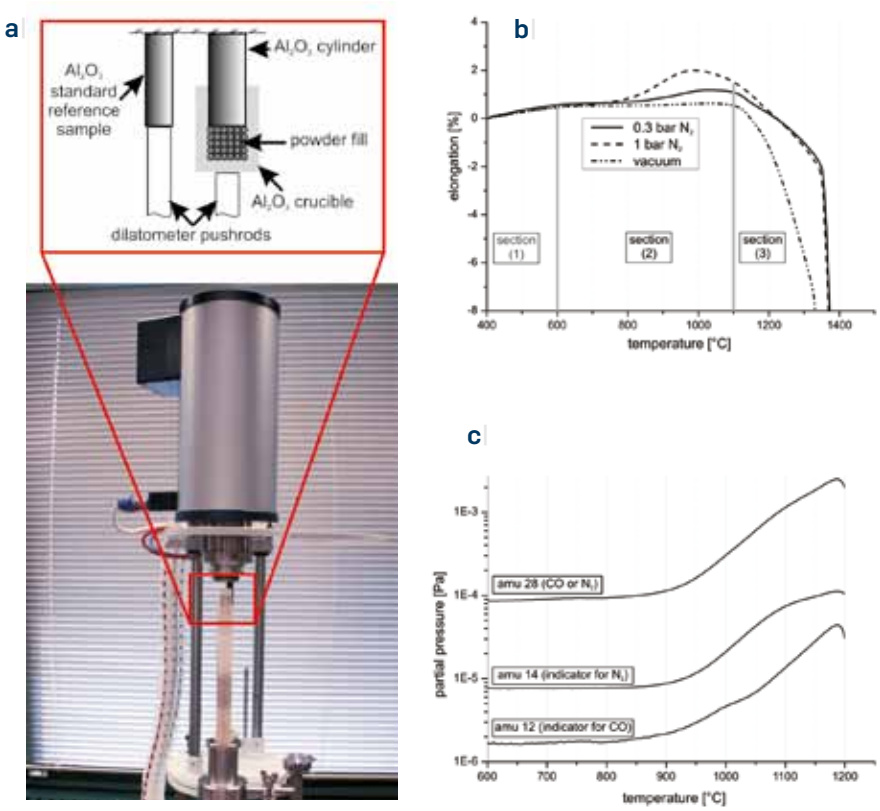


Figure 1: *(a) Vertical dilatometer Linseis L75PT and schematic drawing of the experimental procedure; (b) Results of dilatometric measurements of Fe-CrMnCN powder in vacuum, 0.3 bar N_2 and 1 bar N_2 respectively. In section (1) volume changes of the filling arise from thermal expansion of the material. Nitrogen uptake, lattice expansion and the formation of nitrides result in a volume increase in section (2); The behavior in section (3) is dominated by dissolution of nitrides, solid state sintering and later the formation of the liquid phase; (c) Results of residual gas analysis during continuous heating of the Fe-CrMnCN powder in vacuum atmosphere. Reduction of the surface oxides is measured to start in the temperature range of 800°C–900°C. At T > 950°C degassing of nitrogen is detected.*

Gaseous nitrogen is widely used in metallurgical processes. The purpose of the application can be fundamentally different, depending on the material, target properties of parts and the process temperature. Below approximately 900°C nitrogen is known to be a protective gas. However, at higher temperatures thermodynamic stability of N2 molecules decreases and the atmosphere becomes active. Based on this effect the SolNit® (Solution Nitriding) process was developed and is currently used in industrial production to enhance the surface properties of iron-based parts exposed to wear and corrosive attack, e.g. pump impellers or polymer extruders. The aim of this procedure is a surface modification of the products by increasing the nitrogen content. SolNit® is carried out at temperatures between 1050°C and 1150°C using pure nitrogen as an atmosphere. One other application field for N_2 is related to the powder metallurgical production route. In this case nitrogen is not only used to protect the metallic surface from oxidation, but also to adjust a desired N-content of the parts. The latter is carried out to optimize the sintering parameters and thus to reduce

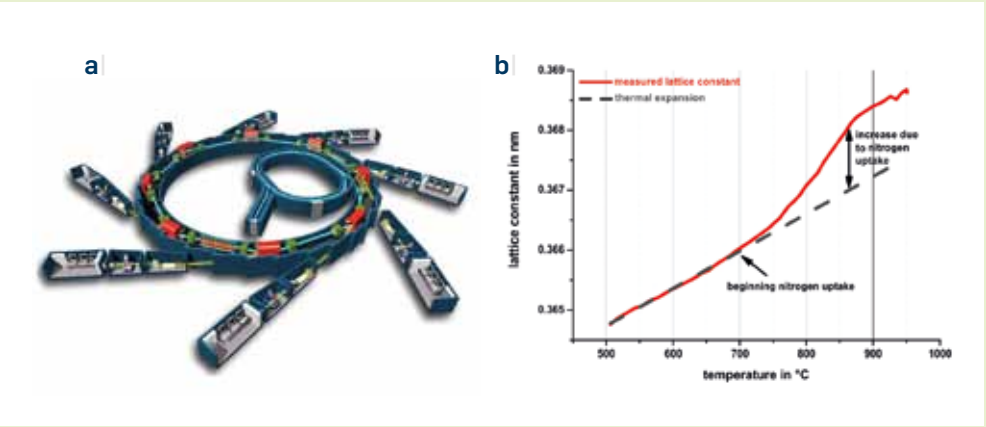


Figure 2: (a) Sketch of a synchrotron storage ring (courtesy of EPSIM 3D/JF Santarelli, Synchrotron Soleil) ; (b) Lattice constant of an Fe-CrMnCN steel powder heat treated under nitrogen atmosphere. The linear increase is caused by thermal extraction as indicated by the dashed line. Starting at 700°C, the lattice constant increases significantly due to nitrogen uptake.

the processing costs or to prevent a degassing of alloyed nitrogen at higher temperatures. For instance, the optimal densification temperature of a vanadium-rich cold work tool steel in the so-called Super-Solidus Liquid Phase Sintering (SLPS) process can be lowered by up to 100 K in comparison to sintering in vacuum. Furthermore, in case of steel powders prealloyed with N, it is essential to avoid the undesired loss of nitrogen. This effect is likely to occur at elevated temperatures in vacuum atmosphere and can be prevented by an appropriate nitrogen partial pressure.

In this context, gas-solid interactions of highly alloyed steel powders and the surrounding atmosphere during Super-Solidus Liquid Phase Sintering are investigated at the Chair of Materials Technology. Special focus is set on the influence of atmospheric conditions and surface reactions on microstructural changes, constitution and densification behavior of gas-atomized steel powders during the sintering cycle. One effective experimental device is the vertical dilatometer with attached residual gas analyzer. Due to the upright arrangement, investigations can be performed on loose powder fillings without precompaction, presintering or use of binders (Figure 1, a). Measurements of volume changes as a function of temperature provide information about thermal expansion, reordering of the powder grains, phase transformations and sintering behavior of the material (Figure 1, b). Correlation of these results with the experimental outcome of residual gas analysis (Figure 1, c) enables the extraction of the sintering response of the powder filling on the reduction of surface oxides.

Time-resolved information about the crystallography can be derived from energy dispersive diffraction (EDD) of synchrotron radiation for different temperatures and atmospheres (Figure 2, a). Experiments were conducted at the synchrotron storage ring BESSY II in Berlin using an Anton Paar DHS 1100 high-temperature stage. Steel powders were continuously heated with a rate of 10 K/min in nitrogen and helium atmosphere, respectively. Temperature and time-resolved information about phase transformation and the formation of new phases can be determined. Furthermore, detailed analysis of lattice constants of individual phases allows conclusions about the amount of interstitially dissolved elements and thereby about the temperature at which the absorption of nitrogen starts (Figure 2, b).

Within the scope of the project, the presented investigation techniques are combined with thermodynamic equilibrium calculations as well as X-Ray Photoelectron Spectroscopy and Scanning Electron Microscopy, to achieve fundamental understanding of the complex processes taking place at the surface and in the bulk of highly alloyed steel powders during sintering in different atmospheric conditions.

Dr. Stephan Huth
Juniorprofessor for Materials in Hydraulic Fluid-flow Engines
Email: huth@wtech.rub.de

Dr. Sebastian Weber
Material Technologies
Email: weber@wtech.rub.de

Prof. Dr. Werner Theisen
Material Technologies
Email: theisen@wtech.rub.de

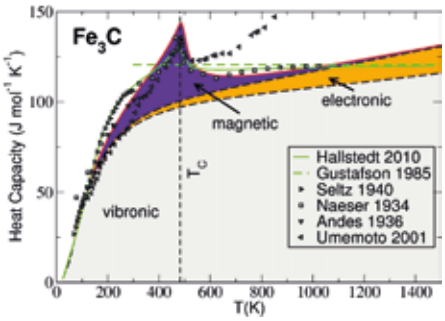


Figure 1 Calculated heat capacity of cementite (red line) in comparison with available experimental data (open symbols). The calculated quasiharmonic, electronic and magnetic contributions are shown in grey, orange and blue, respectively. Based on the ab initio results, the traditional thermodynamic assessment (green dashed line) has been significantly improved (green solid line).

The research in the group "Computational Phase Studies" of Dr. Tilmann Hickel at the Max-Planck-Institut für Eisenforschung is devoted to the physics of (meta) stable thermodynamic phases in metals and transitions between them. A major aim is the **theoretical prediction of thermodynamic bulk phase diagrams**, due to the direct relation to many technologically relevant properties and processes in metals. The group aims at a full ab initio derivation of these properties, mainly making use of density functional theory (DFT). In this context, many methods have been developed, extended and applied to advanced material systems, including:

- The calculation of all relevant free energy contributions, the application to industrially relevant materials, and the combination of the results with thermodynamic databases.
- The description and prediction of temperature and stress induced phase transitions and/or structural changes in shape memory alloys, steels and related materials.
- The energetics and kinetics of alloying elements, impurities and defects, and their relevance for embrittlement phenomena, precipitation and ductility of materials.

In order to **derive free energies from first principles**, one needs to combine DFT with thermodynamic concepts. For many unary metals already the quasiharmonic approximation, including electronic excitations, yields remarkable agreement with experimental data. For several material science questions, however, an extension of the methodology is necessary. For example, we were able to resolve the question about dominant free energy contributions of a material close to its melting point only by considering anharmonic lattice vibra-

Ab initio based prediction of phase diagrams:

Application to magnetic shape memory alloys

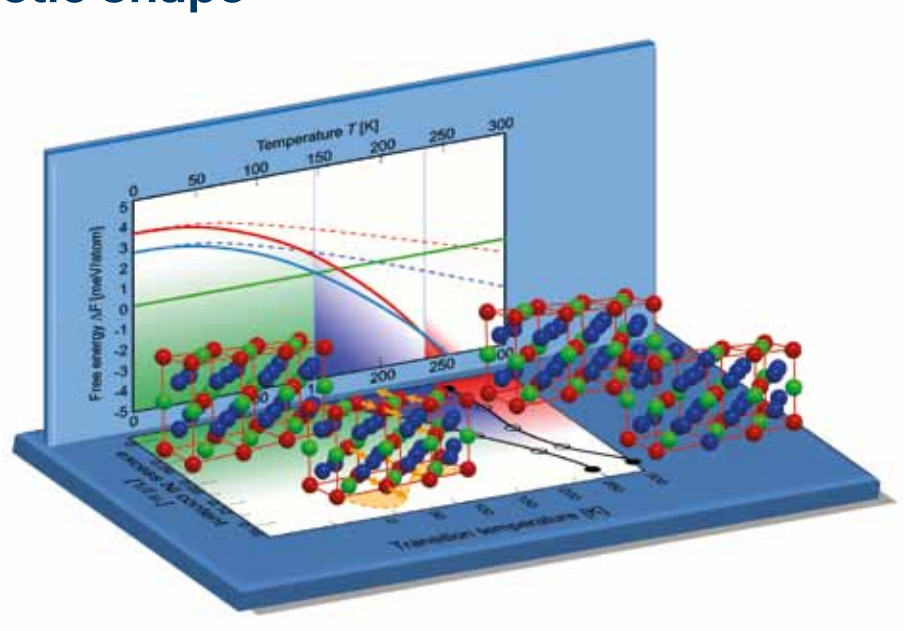


Figure 2: Ab initio prediction of the phase diagram of $Ni_{2+x}Mn_{1-x}Ga$. Upper panel: The free energies of the martensite (green line - reference), austenite (red line) and premartensite (blue line) have been determined. Only the solid lines take magnetic excitations into account, whereas this is not the case for the dashed lines. Lower panel: The transition temperatures derived from the intersections of the free energies are plotted as a function of x.

tions and entropically stabilized vacancies. For steels, the **magnetic excitations** form the most challenging contribution, both with respect to methodological and numerical concepts, due the long range interactions and spin-quantization. After having derived analytical approaches to obtain the magnetic heat capacity of bcc iron up to the Curie temperature, several schemes based on classical and quantum Monte Carlo (MC) simulations have recently been developed, carefully explored and finally used. A typical example is the heat capacity of the precipitate phase cementite, for which the experimental investigation resulted in a large scatter, whereas our MC approach allowed us to identify the correct temperature trends (Figure 1). These results have been used for an improved Calphad assessment of the Fe-Mn-C phase diagram[1].

Ferromagnetic shape memory alloys of the Heusler type, such as the Ni-Mn-Ga system, are characterized by a phase diagram including magnetic as well as structural phase transitions. To perform a systematic search for improved alloys (allowing, e.g., applications at room temperature), however, a thorough understanding of the physical mechanisms driving the phase transitions and their chemical trends is required. We have, therefore, used our first-principles methods to explicitly compute all entropic contributions that are relevant for the stabilization of the involved phases.

In a first step we have investigated the **phase stabilities** of the stoichiometric compound Ni_2MnGa. Phase transitions were already observed if no magnetic excitations are considered (dashed lines in Fig. 2). In this case the martensite (green line, taken as a reference) becomes thermodynamically unstable with respect to the formation of the pre-martensite (blue line) at temperatures above 200 K, but the transition from the pre-martensite to the austenite is not reproduced. This situation changes completely if magnetic excitations are considered, making the austenite the stable phase at a temperature of approx. 240 K and stabilizing the pre-martensite faster relative to the martensite. We therefore conclude that the sequence of phase transitions in the Ni-M-Ga system is a result of a **delicate interplay of vibrational and magnetic degrees of freedom** in these alloys[2].

In a second step, the approach has been generalized to supercells representing other compositions in order to investigate chemical trends. We find an increase of the martensitic phase transition temperature with x in $Ni_{2+x}Mn_{1-x}Ga$ and revealed a sensitive dependence of this behavior on the Curie temperature of the system. Furthermore, a strong dependence of the pre-martensitic phase stability on the Ni content was resolved. Similar investigations have been performed for the $Ni_2Mn_{1+y}Ga_{1-y}$ system and other chemical compositions. Employing sophisticated interpolation schemes for the free energies, the supercell results have been used to **predict the phase diagrams for Ni-Mn-Ga** based magnetic shape memory alloys. The thus achieved insights into the nature of phase stabilities in Heusler alloys can be used as a road map to obtain shape memory materials with tailored thermodynamic properties.

[1] *B. Hallstedt, D. Djurovic, J. von Appen, R. Dronskowski, A. Dick, F. Körmann, T. Hickel, J. Neugebauer: Calphad 34 (2010) 129-133.*
[2] *M. Uijttewaal, T. Hickel, J. Neugebauer, M. Gruner, P. Entel: Phys. Rev. Lett. 102 (2009) 035702.*

Dr. Tilmann Hickel
Computational Phase Studies, MPIE Düsseldorf
Email: hickel@mpie.de

Improved VUV light conversion phosphors from task-specific ionic liquids

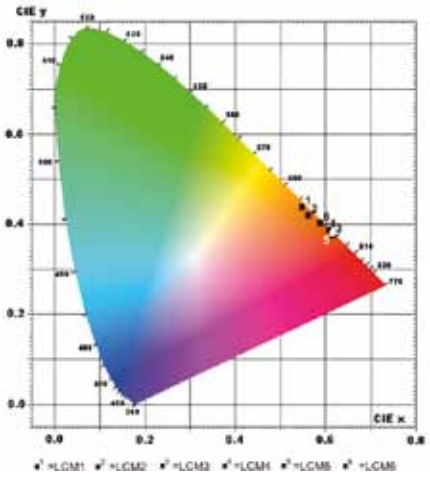


Figure 1: Ionic liquids for the manufacturing of quantum-cutting and down-converting phosphors.

The availability of electric energy is one of the key demands to sustain human needs. Currently the USA, the European Union and China are the countries with the largest electric energy consumption and the demand for electric energy is rising throughout the world. Considering that 19 % of the total generated electric energy is currently used for lighting purposes and energy costs are rising and society's environmental awareness increases, a more efficient electric energy management is desired. The USA, the EU and other countries are successively banning traditional incandescent lamps to reduce energy wastage. Despite the progress of light emitting diodes (LEDs), to date compact fluorescent lamps (CFLs) are the most popular replacements for the classical incandescent lamp. In contrast to incandescent lamps which emit a continuous light spectrum, in CFLs UV radiation generated by a mercury plasma is converted to visible light by lanthanide-based phosphors. However, the use of mercury gives rise to severe human health and environmental issues and it would be desirable to replace mercury with less toxic and environmentally more benign materials such as xenon. Unfortunately a xenon-based technology suffers from two major drawbacks: a slightly reduced efficiency of the discharge process and, more importantly, the higher energy VUV emission of the Xe plasma. The latter implies a substantial intrinsic energy loss. This could be overcome by the development of new phosphor materials which convert VUV photons to visible photons more efficiently. For this a quantum cutting process, realized via down-conversion, has been suggested where, in principle, the efficiency could be increased up to 200 % by splitting a high energy VUV photon into two photons of less than half the energy. Using such phosphors excited through a xenon discharge process, would solve the environmental and health issues of CFLs and even further improve the energy efficiency. However, in contrast to up-conversion, down-conversion processes in nanomaterials are scarcely studied. We started to study down-conversion in the nanoscale with the most prominent Gd-Eu quantum cutting couple in order to develop and improve a synthesis method gaining to access pure, quenching-species free materials with excellent photophysical properties. Our new approach is to employ ionic liquids as the synthesis medium, nanoparticle-stabilizer and reaction partner. Ionic liquids as salts with a melting point below 100 °C (many of them are liquid at room temperature and below) are currently receiving rising interest for applications in nanomaterial synthesis. Employing ionic liquids with complex fluoride anions we succeeded in the preparation of pure, oxygen-free GdF3:Eu. To improve the physico-optical properties of the luminescent material, we applied different ionic liquids and different preparation methods to check for the material with the highest performance. Powder X-ray diffraction shows that hexagonal and orthorhombic GdF3 material was obtained, depending on the ionic liquid used. Transmission electron microscopy reveals the minute size of the obtained particles and the various morphologies obtained when applying different ionic liquids (Fig. 2). Thus the materials' properties can be tuned by varying the reaction conditions.

The quantum cutting abilities were examined depending on the concentration of the Eu3+ ions and the reaction conditions. We found that the best Eu3+ concentration in GdF3:Eu is 5 %. For this material, a quantum efficiency of 145 % was determined according to the formula proposed by Meijering et al.[2]. Taking this concentration and changing the ionic liquid in the synthesis route, allowed enhancing the quantum efficiency significantly, and values ranging from 130 to

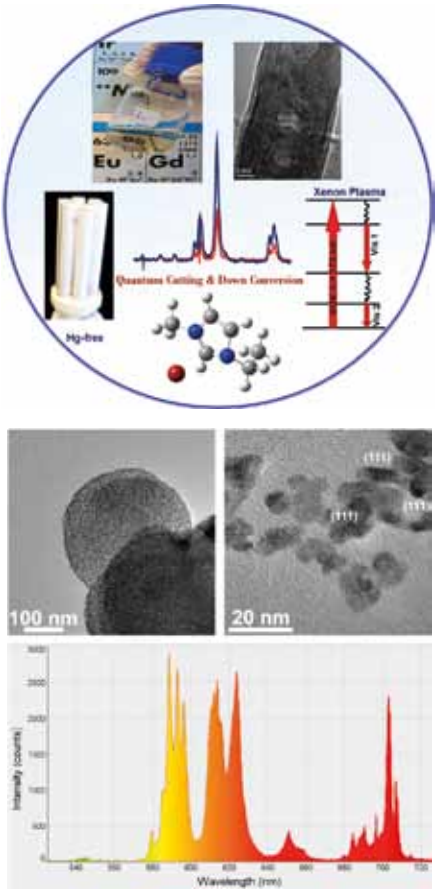


Figure 2: Representative TEM micrographs of various GdF3:Eu 5% materials (top left), emission spectrum (bottom left) and CIE colour coordinates for GdF3:Eu 5% in various ILs at RT.

190 % were obtained. Thus, we were for the first time able to obtain a quantum cutting efficiency close to the theoretical limit with particles of an average size of 6 nm. In conclusion, the ionic liquid-based synthesis route turns out to be a very efficient method to obtain pure, oxygen and quenching-species free, nanosize fluoride materials [1,3,4]. We were able to obtain different phases, morphologies and quantum cutting efficiencies close to the theoretical limit, tuned by the used ionic liquid.

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Chantal Lorbeer, Dr. Joanna Cybinska, Dr. Pushpal Ghosh, and Prof. Dr. Anja-Verena Mudring
Institut für Anorganische Chemie I
Email: anja.mudring@rub.de

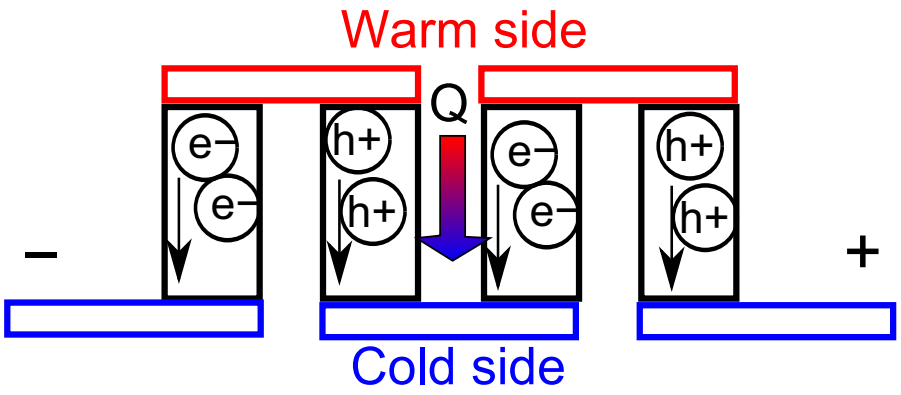

Figure 1: Illustration of a thermocouple where the charge carriers and heat all flow in the same direction two different types of semiconductor material.

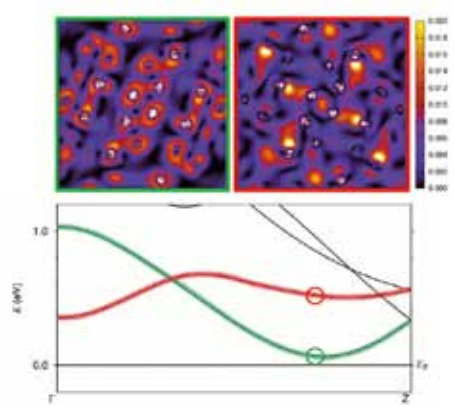

Figure 2: Lowest conduction bands of ZnSb. The valence electron density from the two states in colored circles is also shown.

Thermoelectric materials

Decreasing fossil fuel supplies and increasing greenhouse emissions make the need for sustainable energy sources and increased energy efficiency urgent. In converting waste heat to electric power, thermoelectric materials can improve the energy efficiency of combustion engines or harvest the energy from sunlight. With between 50–70% of the energy from burning fossil fuels being lost as waste heat, thermoelectric materials can play an important part of the solution to our energy challenges.

Almost all thermoelectric devices are based on the concept of a thermocouple, Fig. 1. By forming a junction between pellets of *n* and *p*-type conductor, it is possible to have heat moving in one direction and the generated charge flow in series. Using these properties of the thermocouple, it is possible to team up pellets to create thermoelectric modules. These devices can not only act as generators of electric current, but are also suitable as heat pumps.

A material's suitability for thermoelectric application is measured by the dimensionless figure of merit

$$zT = (\sigma T/\kappa)S^2$$

where S is the Seebeck coefficient and σ and κ are the electronic and thermal conductivities respectively. zT determines the fraction of the Carnot efficiency which can be achieved by a thermoelectric material and one must therefore maximize the power factor $S^2\sigma$ and minimize κ. Apart from zT, several considerations, such as cost, non-toxicity and manufacturability, must be taken to account for a material to be technologically relevant.

New materials

The figure of merit for a material will peak at a characteristic temperature and the material of choice will thus depend on the application. A commercially available thermoelectric device will most probably be based on one of the three classic materials, Bi_2Te_3 (20 °C), PbTe (200 °C) and SiGe alloy (1000 °C). As S, σ and κ are coupled and all depend strongly on the detailed electronic structure, carrier concentration and crystal structure, the task of finding new compounds with large values of zT is very difficult. Here we will illustrate three basic ideas, namely band-structure optimization, the 'Phonon-Glass-Electron-Crystal' concept and nano-structuring.

In a one band model the electronic density of states and mean free velocity are inversely proportional. If, however, several bands are found around the chemical potential it is possible to optimize both simultaneously. This is illustrated in Fig. 2 where the band structure of ZnSb is shown. It is seen how the formation of next nearest neighbor bonds leads to multiple minima in the conduction bands.

The idea behind a 'Phonon-Glass-Electron-Crystal' can be illustrated by the stuffed skutterudites, Fig 3. The loosely bound filler atoms scatter the phonons, thereby reducing lattice thermal conductivity, whereas the Sb framework conducts the electrons. The (Fe,Co) ratio can be used to control the number of charge carriers and optimize the power factor.

A different approach to reducing the thermal conductivity is nanostructuring. This can be done either by a "bottom up" approach, where materials self-form inhomogeneities on the nanoscale or by a "top down" approach where materials are processed (e.g., ground) into nanocrystalline pieces which then are sintered or pressed into bulk objects. An example of the first approach is lead-antimony-silver-tellurium (LAST). LAST is synthesized by reaction of $AgSbTe_2$ with PbTe and is found to be a bulk material where nano inclusions of $AgSbTe_2$ rich areas are formed in the AgSbPbmTe2+m matrix. Examples of the "top down" approach are the nano-structuring of SiGe alloys or the high zT found in the *p*-type $(Zr_{0.5}Hf_{0.5})Co(Sb_{0.8}Sn_{0.2})$ half-Heusler Alloy produced by a combination of ball milling and hot pressing.

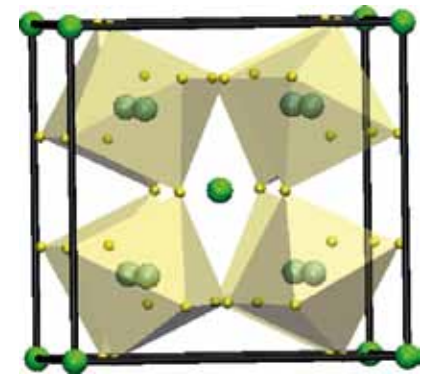

Figure 3: The stuffed Skutterudite structure $La(Co,Fe)_4Sb_{12}$. The framework consists of corner-sharing antimony octahedra (yellow) centered around the transition metals (blue). The Lanthanides (green) fill the voids and form a body centered cubic lattice of loosely bound atoms.

Dr. Georg Madsen
Research Group Leader, Department of Atomistic Modelling and Simulation
Email: georg.madsen@rub.de

Short News

International Student Tandems

A new program at the Chair for MEMS materials (Prof. A. Ludwig) for the international scientific cooperation of students was funded by the Rectorate of RUB. The idea is to build international student tandems. This means two students – one from RUB and one from an international partner institution – work closely together on a joint research topic in the area of combinatorial materials science. E.g. an international student will come to RUB for 6 months to work together with a RUB student, and after this period the international student returns to their home institution together with the RUB student to continue the work on the joint research project. With this, the students get international scientific experience and have a good chance, not only to make their Bachelor or Master thesis, but also to participate in a publication.

Prof. Dr. Alfred Ludwig
MEMS materials
Email: alfred.ludwig@rub.de

Master's Course Materials Science and Simulation – MSS

In recent years theoretical and practical knowledge in numerical methods has proven to be one of the most decisive key competencies of nationally and internationally successful materials scientists and this development is still continu. The RUB meets this need for material scientists trained in numerical simulation and experimental characterization and processing techniques by the Master of Science programme "Materials Science and Simulation". The programme focuses on providing students with a thorough knowledge in materials science and numerical methods. Furthermore it will enable them to apply practical skills and knowledge in experimental settings already during their studies. Therefore, graduates will be able to obtain sustained knowledge and competences and thus have the best prerequisites to meet the challenges in their future industrial or scientific work environment. The new Master's Course will lead to a 'Master of Science (MSc)' degree and provide students with:

- a comprehensive knowledge of materials science, physics and numerical methods,
- practical experience and the necessary theoretical background in applying modern numerical and experimental methods on all relevant scales,
- competence to plan and conduct key experiments in modern characterization and processing techniques,
- the ability to apply advanced modelling and simulation methods,
- the build-up of research competence by planning and conducting research projects,
- a thorough understanding of the interrelation between processing, structure and properties of materials,
- hands-on experience in project-oriented teamwork, project management skills and interdisciplinary communication.

The 2-year international Master of Science programme is offered by the engineering department of the RUB. Courses will be held in English by internationally recognized experts from the Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), the Institute for Materials, the department of civil engineering, and the department of physics. The programme is addressed to students who hold a Bachelor's degree in engineering, natural sciences, applied mathematics or computer sciences.

- *Contact: mss@icams.rub.de*
- *Further information can be found at the ICAMS website: www.icams.de/mss*

Prof. Dr. Alexander Hartmaier
Micromechanical and Macroscopic Modelling
Email: alexander.hartmaier@rub.de

Materials Research Department

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Publisher:
Materials Research Department
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Contact:
Ruhr-Universität Bochum
Materials Research Department
Prof. Dr.-Ing. Alfred Ludwig
Universitätsstraße 150
D-44801 Bochum
Building IA, Floor 1, Room 151
Tel.: +49 (0)234 / 32-27492
Fax: +49 (0)234 / 32-14409
Email: mrd@rub.de

Design:
jungepartner.de

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