



PART II.

THE DEPARTMENTS

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Department of Computational Materials Design

J. Neugebauer

Scientific Concept

The objective of the department is the development and application of **computationally efficient yet accurate multi-scale techniques** that are able to link the predictive power of *ab initio* approaches to the macroscopic scale, as relevant for designing and understanding structural materials for engineering applications. With increasing structural and chemical complexity of next generation steel grades the availability of theoretical/computational tools to perform all major steps in the design, analysis, or identification of synthesis routes will become more and more decisive. Only then the desired targets with respect to mechanical behavior, thermodynamic and mechanic stability or resistance against aging, corrosion or failure can be achieved.

Since the department became operational in summer 2005 it started a number of activities in that direction. One branch of activities, headed by T. Hickel, was the development of numerical tools that allow an **extremely accurate determination of all free energy contributions** by *ab initio* techniques, i.e., without having to rely on experimental input or fitting data [1]. Being able to compute highly accurate free energies opens the door to compute materials properties or kinetic processes solely on the computer. While initially applications were limited to simple bulk systems (such as non-magnetic fcc metals) enormous methodological progress allows the department now to apply these methods to real-world highly complex materials such as TWIP or TRIP steels. The methods have reached a maturity and accuracy that rival and often exceed calorimetric measurements [2,3]. Achieving *ab initio* error bars that are below the experimental ones is quite unique in solid state physics. The precision, achieved by our methods, has been successfully used e.g. to assess experimental data entering thermodynamic CALPHAD-based databases.

Another major achievement, pushed forward in the group of M. Friák, was the development of approximate but fast multi-scale methods that allow a **quick screening of materials properties**. These scale-bridging methods which connect DFT with various homogenization approaches or Ashby concepts proved

highly successful in identifying optimum chemical alloy compositions, e.g., to tailor elastic properties, in uncovering hidden rules and limitations of alloys [4], or in guiding experiments e.g. in the MA department to minimize the number of samples that need to be synthesized [5]. Both approaches – extreme accuracy and fast screening – started with the initiation of the department. While in the beginning both were developed separately, the massive methodological progress achieved over the last years allows more and more often to use a combination of both and to tackle challenging materials science problems, which would be out of reach when applying a single method only.

Further cornerstones of the department, again from the very beginning, are the operation of a **high-performance computer cluster** and our in-house developed **multiscale library SPHInX** [6,7]. The 2011 newly installed computer cluster consists of 5500 cores and was ranked like its predecessor in the international Top-500 list of supercomputers. To maximize computer resources, great care has been devoted to optimize the software and to adopt it to our specific needs (see also p. 19). Both the computer cluster as well as the development of the SPHInX library are coordinated by C. Freysoldt.

C. Freysoldt is also head of the group “Defect Chemistry and Spectroscopy” devoted to non-metallic systems such as e.g. oxides. Oxides play a crucial role on steel surfaces and are fundamental to understand corrosion or coatings. Due to the existence of an electronic bandgap an accurate treatment of these materials requires to go beyond approaches that work well for metals. The group is therefore highly active and internationally well known for its method development [8]. Together with M. Todorova, who heads several projects on surfaces and electrochemistry, the group provides a strong link to the experimental and theoretical activities on oxide surfaces, electrochemistry and corrosion in the GO department.

Newly established groups complement the expertise of the existing activities. In 2010 the department was successful in appointing R. Spatschek as head

of the group “Mesoscale Simulation”. In the last two years the group has been highly successful in connecting to the existing in- and out of house activities and in establishing a strong research program. For example, within the Sfb “Steel - *ab initio*” (see p. 26) the group was able to transfer the concept of an attractive H-H interaction, which is crucial to understand H-embrittlement, from the atomistic to the continuum scale in an almost lossless approach, i.e., without having to make sacrifices in the accuracy [9]. This allowed to derive complete phase diagrams, which would not have been computationally affordable if only atomistic methods were used.

Very recently (April 2012), the department has attracted B. Grabowski from the Lawrence Livermore National Lab in the US as head of the new group “Adaptive Structural Materials”. The group is financed by an ERC grant awarded to D. Raabe and J. Neugebauer and has a unique structure: It is a joint *ab initio* and experimental group and headed by an experimentalist (C. Tasan) and a theoretician (B. Grabowski). The main aim of the group is to develop concepts of how originally unstable phases may be used to synthesize smart structural materials with a microstructure that dynamically adapts to external loads. This adaptivity can be used to design mechanically superior alloys as shown e.g. for TWIP/TRIP steels.

In the reporting period there had been also changes in the group structure. A. Dick, who headed the group “Precipitation and Kinetics”, got an attractive offer as vice president at an institute of the National Academy of Sciences of Belarus and left the institute. L. Lymperakis, head of the Microstructure group for several years, received a prestigious EC grant to build up a research group in his home country at the University of Thessaloniki. He stays in close contact with the department and institute and supervises a number of projects (see p. 48). J. von Pezold, who followed L. Lymperakis as head of the “Microstructure” group, had to leave the department for family reasons. The majority of the projects initiated and supervised by him have been transferred to the group of B. Grabowski, where they ideally fit due the group’s strong focus on microstructure.

While each of the groups in the department has a high individual visibility, specific expertise and methods, the complementary character of the methods provides many successful opportunities for collaborations and resulted in several granted projects and scientific breakthroughs. Examples are the work on H-embrittlement, where three groups are involved (Hickel, Pezold/Grabowski, Spatschek) or on point defects where unique insight could be obtained by combining the metal and semiconductor community (Hickel, Grabowski, Freysoldt) [8]. Another major group bridging activity is the development of a Python-based library that automates time consuming

and error prone tasks such as constructing input files for high-throughput calculations, job submission, collection of input and output data in unified databases and analyzing and visualizing the often huge output data files. The library is highly adaptive and allows to easily incorporate existing software tools such as e.g. the department’s 3D-lab which enables interactive exploration of complex crystal structures, phase transitions or defects (Aydin, Hüter, Witt, Hickel, Spatschek). The library provides also an excellent basis to build stand-alone software tools for specific materials science modeling tasks. An example is the SC-EMA tool (see Fig. 8) that provides a graphical user interface and all algorithms to compute the elastic moduli of polycrystalline materials from *ab initio* single crystalline elastic tensors (Titrian, Aydin, Friák).

The collaboration with ICAMS in Bochum has been further intensified resulting in joint publications (e.g. on the topic of H-embrittlement; [10]), conference contributions and conference symposia (e.g. a symposium on Thermodynamics at the Multiscale Materials Conference 2012 in Singapore with I. Steinbach, a symposium on Modeling Mechanical Properties with A. Hartmeier, or ADIS 2010 and 2012 and a DPG symposium 2013 on High-Throughput Methods with R. Drautz). Several members of the department (Hickel, Lange, Neugebauer, Spatschek) actively support the newly established ICAMS master course “Materials Science and Simulations (MSS)” at the Ruhr-University Bochum by giving courses e.g. on quantum mechanics, thermodynamics and statistical physics, or implementing *ab initio* techniques.

The maturity in the theoretical/computational methods achieved by the department groups provides a solid basis for joint activities with experimental groups in house and with industrial partners. The predictive power of these methods not only allows to explain/interpret experimental observations but has reached a new level allowing to make specific predictions regarding compositions or mechanisms that can be verified by experiment. Weekly joint meetings between members of the MA and CM department on various focus topics and dynamic collaborations between groups and members of the departments provide an ideal basis to combine “hot” experimental/technological questions with newest theoretical concepts. These collaborations work very successfully and several examples are given in the highlight articles (p. 101, 105, 107, 111, 113) and joint publications [4-5, 11-16].

A major aim of the department is to bring together the engineering and physics/chemistry community in the field of structural materials and to raise awareness about the specific challenges and developments. Members of the department have been therefore actively involved in organizing workshops, conferences or symposia in both communities (see p. 166). For example, our conference series “*Ab initio* description

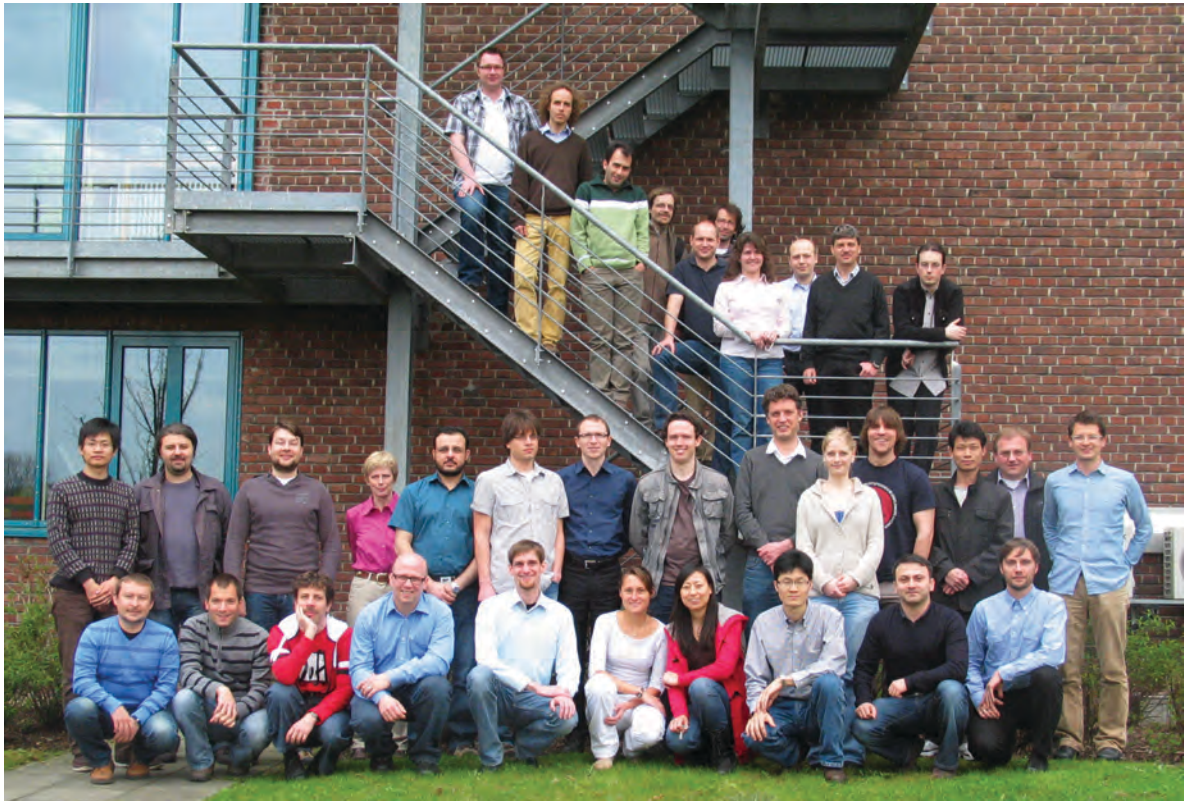


Fig. 1: The CM department (summer 2011).

of iron and steel (ADIS)” is the leading one on this topic and attracts always the top experts from both communities. The latest one, taking place in April/May 2012 at Ringberg Castle (Tegernsee), had a specific focus on most recent developments and successes in modeling thermodynamic and kinetic aspects in steels. Another example are symposia organized by the department at the German Physical Society meeting on steel and multiscale topics that show the enormous theoretical challenges in describing physically and structurally complex systems such as steel and that help to interest and recruit physicists in these topics. Related to these activities the head of the department (J. Neugebauer) has been elected as chair of the division “Metals and Materials” for the years 2013-2016.

Due to the high visibility of the scientific work members of the department received a large number of invited talks at the major conferences in the field, such as TMS, MRS, MMM, Calphad, DPG. The high scientific standards provided also the basis for successfully extending e.g. the joint RWTH-Aachen-MPIE SFB “Steel – *ab initio*” and acquiring prestigious research grants such as the above mentioned ERC grant, as well as many other national (DFG, BMBF, AvH) and European grants. Members of the group received also prestigious prizes. For example, F. Körmann received the Otto-Hahn medal of the Max-Planck society for his outstanding PhD thesis on the *ab initio* thermodynamics of magnetic systems.

C. Race received an esteemed research grant from the Humboldt foundation for his highly original proposal on grain boundary kinetics.

In the last couple of years the department has grown substantially, from originally about 10 to now more than 40 members. To provide an infrastructure that connects the often very different scientific activities, the department organizes several regular weekly seminars, department retreats and social events. This allows each scientist to get an overview of all existing activities, the available and newly developed approaches and to identify contact partners for collaborations. At the department retreats, which are organized once a year, every student and scientist gets the opportunity to present results and to discuss them with members of the department as well as with our collaborators at ICAMS and other universities who traditionally join these meetings. Members of the department have been also very active in supporting the institute and its activities in the public. For example, T. Hickel scientifically coordinated the activities of the department at the ThyssenKrupp Ideenpark (see Fig. 2), a two week event where the public and specifically children are provided a hands-on experience on what makes materials science so exciting and important in modern society.

In the following the activities of the department groups and of selected project groups are briefly summarized.



Fig. 2: Together with the RWTH Aachen, the MPIE demonstrated at the ThyssenKrupp-Ideenpark the concepts of a tailored materials design. 3D computer simulations (here explained by B. Grabowski, background) have been combined with basic knowledge on crystal structures and mechanical loading experiments (here demonstrated by T. Hickel (left) and C. Hüter (center)).

Scientific Groups

Computational Phase Studies (T. Hickel)

The group Computational Phase Studies (CPS) is devoted to the physics of (meta)stable thermodynamic phases in metals as well as transitions between them. It is since 2006 part of the CM department. Its major vision is the *ab initio* based prediction of thermodynamic bulk phase diagrams, being directly related to many technologically relevant properties and processes in metals. The scientific performance of the group over the last two years is probably best described by the triad of **continuity**, **consolidation** and **change**:

The overall scientific scope of the CPS group is the **continuation** of the activities and directions established in the previous years. In the last two years the group pushed the full *ab initio* derivation of thermodynamic properties forward, using mainly density functional theory (DFT) with the aim to achieve a high precision for all relevant entropy contributions. A major focus of the group has been and continues to be on the fields **magnetic excitations**, **extended and point defects** and **hydrogen**. The following summaries (as well as some of the scientific highlights) demonstrate the substantial progress in these fields regarding the development of new methods and the

derivation of new insights. As a result also the third party funding for all key projects of the group has been extended after successful evaluations.

The treatment of **magnetic excitations** within the scope of phase studies is still of central interest, since its complexity and numerical challenge makes straight-forward solutions often impossible. It turns out that even well above room temperature it is essential to take the spin quantization into account in order to obtain reliable heat capacities of materials (Fig. 3). By the development of various new techniques spin quantum Monte-Carlo simulations, originally restricted to simple model Hamiltonians, could be generalized to allow for the treatment of realistic spin Hamiltonians (F. Körmann). Using our newly developed approaches it has been possible to achieve impressive agreements of the thermodynamic properties of all unary metals [18] and compounds [2] with experiments, where in particular for chromium new insights on its magnetic behavior became apparent (see p. 149) [19]. Another important issue is the development of methods for the influence of magnetic excitations on other thermodynamic properties such as lattice vibrations. As demonstrated for Fe (F. Körmann), it now became possible to perform



phonon calculations even for the challenging case of paramagnetic disorder (see p. 143) [20]. Several of these activities are performed in close collaboration with ICAMS and its CALPHAD group (S. Fries).

Vacancies are the most prominent **point defects** in metals, due to their impact on thermodynamic as well as kinetic properties. Nevertheless, discrepancies in the vacancy formation energy between DFT and experiment made method developments decisive. This includes a correction scheme to tackle errors in the exchange-correlation functional (R. Nazarov) [21] and a breakthrough in understanding the temperature dependence of the anharmonic contribution to vacancy free energies of formation (A. Glensk, see p. 147) [22]. These activities are performed in cooperation with the ASM group and are part of a research package (PAK 461) on the thermodynamics of Al-Mg-Si-Cu alloys, which has benefited from our *ab initio* input [23] and has recently been successfully evaluated for an extension by another two years.

The thermodynamics of **extended defects** is also considered in the CPS group, mainly focusing on the stacking fault energy (SFE) (see Fig. 4). This energy determines the probability of deformation mechanisms in structural materials. The *ab initio* calculations of the dependence of the SFE on the C content [24] allowed highly interesting predictions on nano-diffusion during SFE measurements and deformations (see p. 105) [16]. In addition the influence of Al or Si [25] and magnetism (I. Bleskov) on the SFE has been studied. These and other *ab initio* results have contributed to the understanding of mechanical properties of high-Mn steels [15] and to the success of the collaborative research center SFB 761 "Stahl - *ab initio*" and its extension by another funding period starting in 2011. Precipitates form another

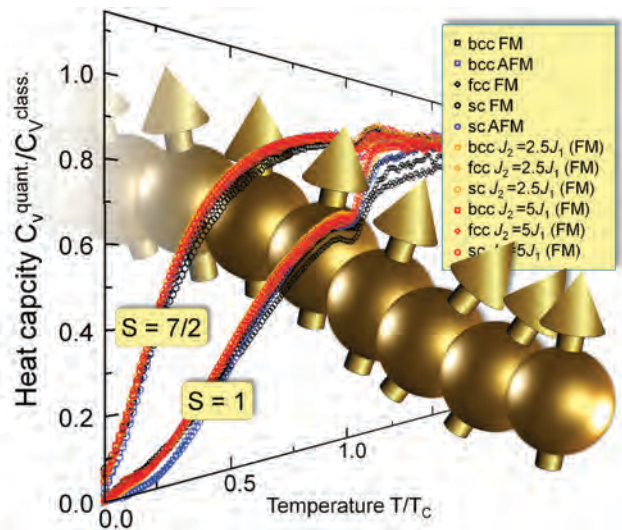


Fig. 3: To compute thermodynamic properties of magnetic materials, it is decisive to take the quantum nature of spins into account. The figure shows the ratio of the heat capacities obtained from quantum vs. classical Monte-Carlo simulations for two different spins S . For a large variety of configurations, this ratio shows remarkably universal temperature dependences. For details see Ref. [17].

class of extended defects, which are investigated in the CPS group. The focus in the group is on the thermodynamic stability of these phases (see e.g. p. 101), their relevance for the overall mechanical properties of the materials (in cooperation with the *Ab initio* Thermodynamics group) and the kinetics of the formation process (N. Tillack, N. Sandschneider). The influence of interfaces and grain boundaries was in the CPS group so far mainly studied in the context of hydrogen migration (see Fig. 5 and p. 119) [10].

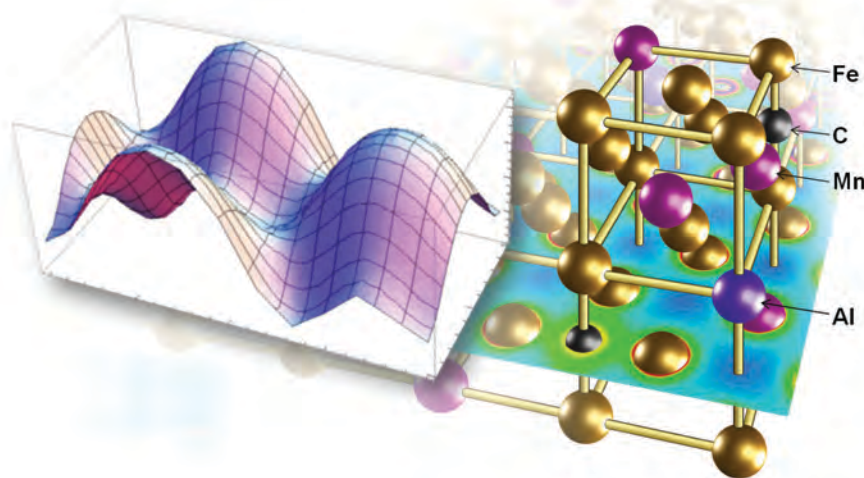


Fig. 4: A major research topic of the CPS group are high-Mn austenitic steels, typically containing up to 20-25 wt.% Mn and a substantial amount of C. To reduce the embrittling effect of H, Al is often added in addition. The deformation behaviour of these materials is determined by the (generalized) stacking fault energy (shown in the inset for non-magnetic fcc Fe). Chemical as well as magnetic trends for the SFE have been systematically studied.



Fig. 5: The interaction of H with planar defects is important for H embrittlement. This figure visualizes a possible diffusion path of H perpendicular to a twin boundary in fcc Fe. The calculations reveal a slight repulsion of the H atom from the defect. For details see Ref. [10].

Hydrogen is relevant for the mechanics of many materials, since it can significantly contribute to embrittlement. The CPS group (U. Aydin, R. Nazarov) therefore made intensive and systematic investigations on the solubility and diffusion of hydrogen in metals [26], including also the effect of superabundant vacancy formation due to hydrogen [27,28]. These activities resulted in an RFCS project on the relation between microstructure and hydrogen embrittlement, coordinated by the head of the group (T. Hickel). In particular the role of hydrogen in advanced high-strength steels is investigated within industrial projects (P. Dey) and the SFB 761 “Stahl - *ab initio*” (A. Chakrabarty). The research benefits from close links to the ASM group, where methods to treat the H-dislocation interaction are developed and the Mesoscale Simulation group, allowing a connection to the continuum scale.

The **consolidation** of the above mentioned activities in the last couple of years resulted in several review articles. The first one was devoted to free energies of point defects [29], a topic which later entered into an extended article on the *ab initio* treatment of defects [8]. Second, a highlight article in the Ψ_k newsletter summarized the developed methods to obtain *ab initio* free energies of bulk phases [1]. A third review describes recent successes in the *ab initio* derivation of phase diagrams using the example of shape memory alloys [30]. The group participated in other reviews on elastic constants [4], semiconductor nanostructures [31], and hydrogen in steels.

All together, the power of the developed set of thermodynamic methods as well as their relevance for materials design are meanwhile accepted well beyond the DFT community. The above mentioned list of key research activities (magnetism, defects, hydrogen) is particularly decisive for **advanced high-**

strength steels, being the reason for several joint research activities with the MA department, but also with partners in other (research and industrial) institutes world-wide. The significant contribution to the understanding and development is not only limited to structural, but applies in a very similar way to **functional materials**. Our long-standing activity in the field of shape-memory alloys, including the prediction of phase diagrams [30,32], has now been extended to their magneto-caloric properties. To perform this work we successfully applied for funding within the priority program SPP 1599 on “Magnetic Cooling”. Furthermore, the links to the **CALPHAD community** are becoming more and more tight. This goes along with an increasing number of examples, which show smaller error bars of *ab initio* derived thermodynamic quantities compared to the scatter in the experimental data. One of the most recent results has been obtained for Ca (B. Grabowski), for which a complete and careful evaluation of all excitation mechanisms and in particular of anharmonic lattice vibrations revealed that a correction of CALPHAD databases is necessary [3]. Due to this kind of developments the head of the group (T. Hickel) is organizing a Calphad Unary Workshop in March 2013 in conjunction with S. Fries (ICAMS).

There have been several **changes** in the personnel structure of the group over the last couple of years. With A. Dick and B. Grabowski two experienced postdocs and driving forces for the research have left the group and became themselves heads of research groups in the CM department. Two other group members have gained so much experience over the last years that they are now taking over more responsibilities in the group: (i) R. Nazarov is becoming continuously more involved in the coordination of all hydrogen-related projects in the group. (ii) F. Körmann, after defending his PhD thesis excellently in 2011, is heading several research projects on magnetic properties of materials.

Two of the PhD students are also taking over responsibilities for the department. (iii) U. Aydin has started with the development of databases and is supervising the colleagues working on a joint (Python based) program package for this purpose. (iv) A. Glensk assists all interested members of the CM department in performing phonon calculations. Other colleagues have recently joined the team: (v) I. Bleskov is now performing the research within the SFB761 and is also responsible for introducing CPA-EMTO methods to the group. (vi) B. Dutta works on magneto-caloric materials and will introduce new methods to calculate phonons for chemically disordered alloys. (vii) X. Zhang will study martensite formation as a Surmat PhD student. (viii) P. Dey strongly supports our understanding of H in high-Mn steels. Finally, there is an ongoing collaboration with O. Marquardt on applications of the k-p formalism [33,34].



Ab initio Thermodynamics (M. Friák)

The group aims at identifying **multi-scale structure-property relations** and uses theoretical methods to identify fundamental mechanisms governing the behavior of materials. The prime motivation is to use scale-bridging concepts (see e.g. Fig. 6) in a theory-guided materials design of new alloys that allows adapting in a fast and flexible way to the often dynamically-changing industrial needs. The **ductility of materials, their strength, and the identification of alternative solutes** are among the key objectives of the group. In order to properly address them, physics-based theoretical methods are combined with engineering phenomenological approaches. These modeling activities are **closely inter-linked with experimental studies** within the MA department as well as outside MPIE.

To predict the **ductility of materials**, we systematically search for suitable figures of merit. An example is our activities in the case of Mg alloys [5, 11] where we connect (i) atomic-scale compositional changes and (ii) an experimentally detected increase in the ductility where yttrium and/or selected lanthanides are used as solutes (see highlight on p. 111 with the MA department - S. Sandlöbes, S. Zaeferrer, and D. Raabe). Our goal is not only to understand how Y and lanthanides additions influence the ductility of Mg but also to suggest which other solutes can possibly be used as more accessible and environment-friendly alternatives to them (L.-F. Zhu, Z. Pei, in coopera-

tion with C. Race, A. Dick, G. Leyson and within the AICES program p. 31).

As far as the **strength of materials** is concerned, solid-solution strengthening of Al has been studied and fundamental anti-correlations between the thermodynamics-governed solubility of solutes and their strengthening impact have been quantitatively described (cooperation with D. Ma and D. Raabe). Employing the volumetric mismatch between the matrix and solutes as the decisive parameter, an optimum volumetric mismatch (that can be connected with specific chemical elements from the periodic table) has been predicted for any given annealing temperature (see Fig. 7).

As one of the recently accomplished **methodological developments**, an open-access web-based application calculating integral elastic response of texture-free multi-phase polycrystalline materials has been successfully implemented (H. Titrian and U. Aydin). The new software tool called SC-EMA (**S**elf-consistent **C**alculations of **E**lasticity of **M**ulti-phase **A**ggregates) is based on an easily extendable Python modular library (www.mpie.de/SC-EMA.html). The package uses single-crystalline elastic constants C_{ij} as input parameters and calculates macroscopic elastic moduli (bulk, shear and Young's) and Poisson ratio of both single-phase and multi-phase aggregates employing self-consistent mean-field methods. Crystallites forming the aggregate can be of cubic, tetragonal, hexagonal, orthorhombic, or trigonal sym-

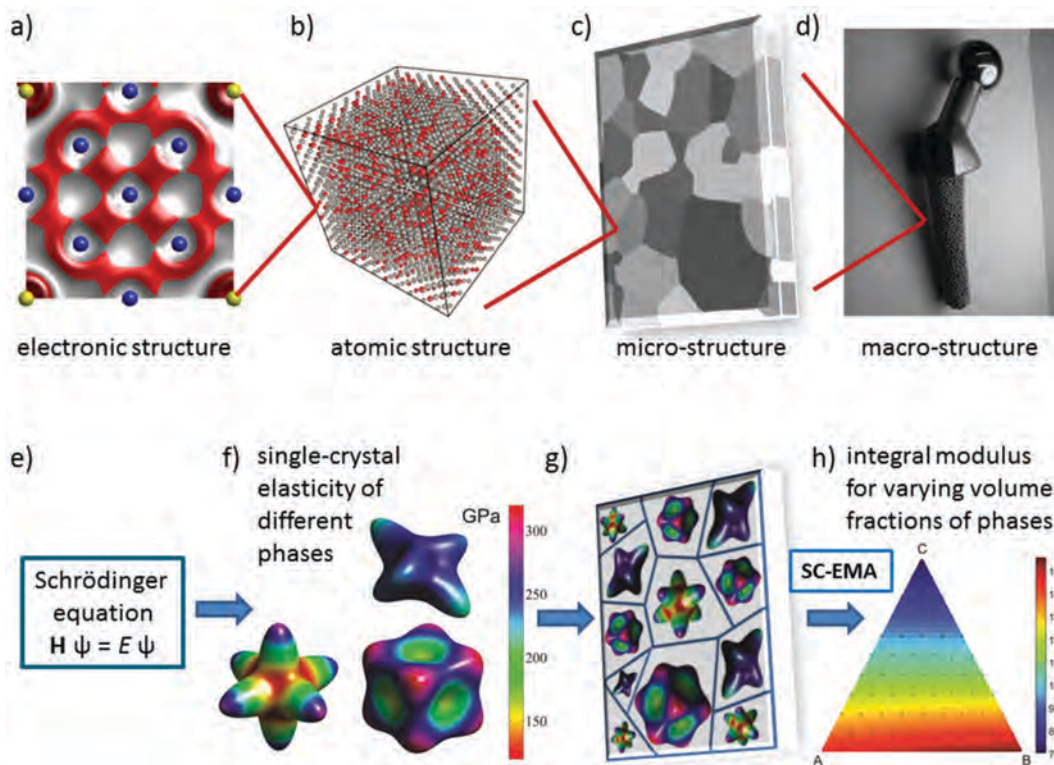


Fig. 6: Relation between the multi-scale structure of a material (a)-(d), represented here by a stainless steel hip-replacing medical implant (d), with the corresponding modeling approaches to determine elastic properties (e)-(h). Part (h) shows a triangular plot of the homogenized Young's modulus of a 3-phase aggregate for different volumetric fractions of phases as calculated and visualized by a newly developed software tool SC-EMA (**S**elf-consistent **C**alculations of **E**lasticity of **M**ulti-phase **A**ggregates), (H. Titrian and U. Aydin).

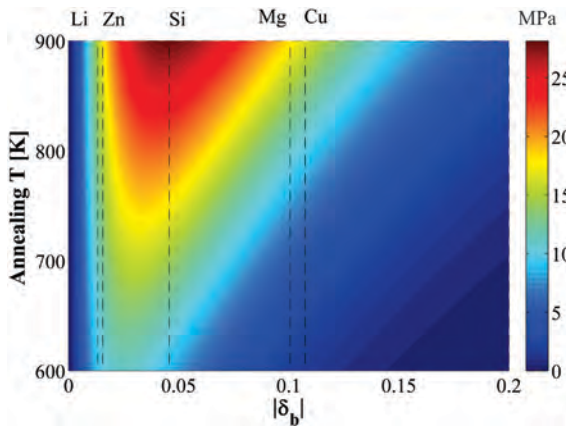


Fig. 7: Color-coded contour plot of the yield stress (in MPa) of polycrystalline Al solid solutions, σ_y measured at 78 K, on annealing temperature T and dimensionless volumetric mismatch $|\delta_b| = 1/a \cdot (da/dc)$ as a function of the lattice parameter a and solutes concentration c (in collaboration with MA department - D. Ma and D. Raabe). Also indicated are volumetric mismatch values corresponding to a few industrially used Al-strengtheners.

metries. In case of multi-phase polycrystalline composites, the shear and bulk moduli are computed as a function of volumetric fractions of phases present in the aggregate (see Fig. 8). The application has built-in criteria that are checking the mechanical stability of phases based on input single-crystalline elastic constants. Elastic moduli are computed together with their bounds as determined by Reuss, Voigt and Hashin-Shtrikman homogenization schemes. From an engineering point of view, the newly developed software probes in a scale-bridging manner fundamental structure-property relations and can be used as a **toolkit for materials-design simulations of alloys with specific macroscopic elasticity**.

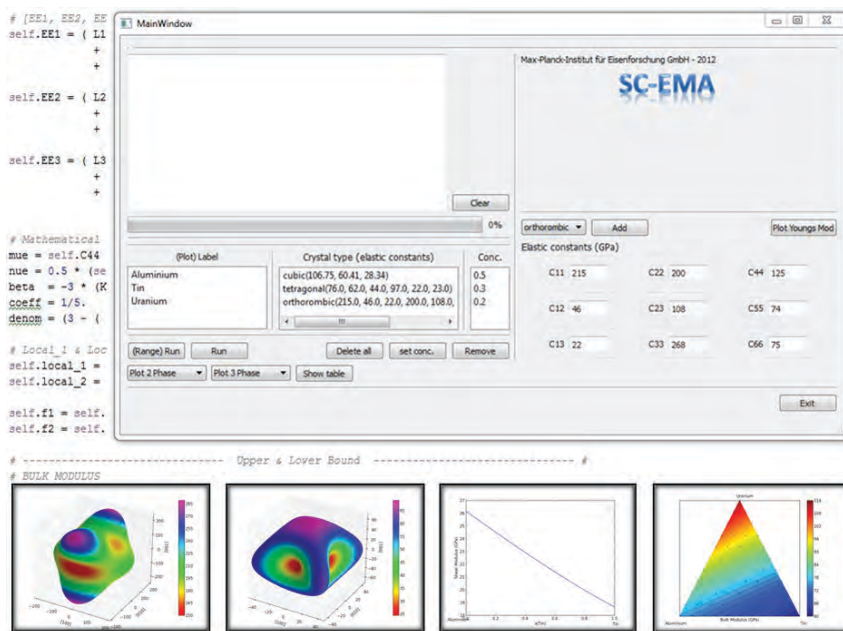


Fig. 8: Screen shots of the newly implemented SC-EMA package intended for analyzing single-crystalline elasticity of crystals with arbitrary symmetry and mean-field calculations of integral elastic response of single and multiple-phase aggregates.

Further research activities focus on e.g. **multi-methodological approaches combining quantum-mechanical and/or atomistic simulations with continuum methods** such as crystal elasticity and crystal plasticity finite element method (CEFEM and CPFEM) together with the MA department, new fast Fourier transforms (FFT) approaches (cooperation with R. Lebensohn, Los Alamos National Laboratory, USA), and phase-field modeling (with H. Emmerich, Bayreuth University), see details e.g. in [12]. As far as various methodological aspects are concerned, different computational methods to the second-order elasticity of cubic crystals were compared and the numerically most robust approach (that also allows for calculating the third-order elastic parameters) was identified [35] (cooperation with D. Holec and P. Mayrhofer from the University of Leoben, Austria).

Ab initio calculations were also applied to a wide range of materials and phenomena, such as (i) changes induced in stoichiometric NiTi allotropes by hydrostatic pressures [36] (together with D. Holec, University of Leoben, and A. Dlouhý, Institute of Physics of Materials (IPM) in Brno, Czech Republic), (ii) the role played by magnetism in martensitic phase transformations (e.g. in Ni, Fe and Co) [4,37] with M. Zelený (Aalto University School of Science, Finland) and M. Šob (IPM and Masaryk University in Brno, Czech Republic), as well as (iii) DFG-funded research focused on two-phase Ti-Fe eutectics [38,39], or Ti-Nb alloys for bio-medical applications [13]. New ways of designing multi-phase materials with extremal strength-to-weight ratios were studied within a biomimetic research aiming at complex hierarchical biocomposites (P. Elstnerová, formerly also with M. Petrov) [14,40] together with H. Fabritius from the MA department, A. Ziegler from the University in Ulm, S. Nikolov from the Bulgarian Academy of Sciences in Sofia, and Z. Střelcová from the Central European Institute of Technology, Brno, Czech Republic. This collaborative DFG-funded project has been successfully defended after the first two-year-long funding period and its extension till May 2013 was approved in early 2011.

The long-term development of the group, that was established in June 2005, can be characterized by systematic building up of knowledge in (i) revealing intrinsic relations between thermodynamic and mechanical properties of materials (jointly with CPS group), (ii) describing the elasticity of materials, earlier only single-phase and ordered ones, subsequently



disordered alloys (together with J. von Pezold and A. Dick) [41] as well as multi-phase composites, and (iii) going beyond the elasticity of materials towards their plasticity that is more important for industrial applications. All this accumulated knowledge has been used to (i) explain trends in existing materials when inter-linking theoretical and experimental studies both inside and outside the MPIE, (ii) explore limits of materials design of new alloys, (iii) establish new multi-methodological connections among different modeling approaches, and (iv) ultimately also design new materials, such as new ferritic steels intended for high-temperature applications developed within the BMBF-funded project “Ferrit950” (a patent application involving MPIE as a co-proposer is pending).

Defect Chemistry and Spectroscopy (C. Frey-soldt)

The group focuses on **atomic-scale defects in non-metallic materials such as oxides, electrolytes, or semiconductors** by means of *ab initio* methods, and develops state-of-the-art methods and concepts for this purpose.

Point defects exert a critical influence on the **electrical, chemical, transport, and other properties** of real materials. Computer simulations are a powerful tool to better understand the formation of point defects, their properties, and their role in modifying macroscopic material parameters. Major challenges in the simulation arise from (i) providing a reliable theoretical framework to accurately compute the defect energetics, notably the formation energy and electrically active transitions within the band gap of the material, (ii) linking the microscopic picture to a coarse-grained theory that is able to describe the experimentally relevant time and length-scale (scale bridging), and (iii) developing useful approaches for point defects in amorphous/disordered materials.

The group heads and coordinates the development of our in-house **multi-scale program package SPHInX**. In the past two years the focus has been on parallelization of key algorithms using MPI and openMP as well as on the public release of the source code (version 2.0) [6]. The MPI parallelization was implemented in collaboration with the MPG Computing Center in Garching, and follows an adaptable single-loop parallelization model. The collaboration revealed again the power and efficiency of the SPHInX modular concept, since the implementation was finished within a few weeks(!) by K. Reuter (GRZ Garching), a plasma physicist by training who admitted to have no real understanding of electronic-structure theory. He highly praised the conceptual clarity of the SPHInX code. Further external collaborators on SPHInX development are Sixten Boeck (Gemmanics IT Consulting, Erkrath) and Oliver Marquardt (Paul-Drude-Institut, Berlin). Recent in-house developments cover a mixed Coulomb-Hook formalism for coarse-graining phonon calculations in

(defective) ionic systems, calculation of energy loss near-edge spectra (S. Zhang), orbital-based energy decomposition using Quamols (B. Lange), and hybrid functionals. Apart from being an efficient platform for method innovation, the SPHInX code is now routinely used for applied research throughout the department.

A unique module in the SPHInX package is the **plane-wave based implementation of k-p theory** that allows to efficiently calculate electronic states as well as strain in semiconductor nanostructures. The implementation offers full flexibility in terms of underlying model Hamiltonian, material composition, and shape of the nanostructure, which are all defined in easy-to-edit input files [33,34]. The code is now being routinely applied – also outside the institute – to a variety of nano-structured semiconductors such as quantum dots, quantum dot arrangements (‘quantum camomilla flowers’), and even to states trapped by the strain fields of extended defects (O. Marquardt, Paul-Drude-Institut, Berlin).

An important aspect of our fundamental research is to provide physically clear interpretations of the quantitative and qualitative results obtained for specific systems. These insights provide important landmarks in guiding applied research towards promising directions. Based on our recent **development of optimized atomic orbitals (Quamols)** [37], that accurately represent the results of highly accurate plane-wave calculations, we are now able to decompose not only wavefunctions and electronic band structures into their atomic contributions, but also the resulting energies. This **new analysis tool** is applicable to a wide range of unsolved question such as the energy distribution in alloys and amorphous materials, surface energies of polar surfaces or the origin of the energetics of defects. Additionally, it provides a very direct and intuitive approach to draw the border line between the bulk and the region nearby the defect that is already modified from its bulk-like behavior. The new approach is also ideally suited to design coarse-grained empirical models for embedding, where the defect region is re-parameterized according to *ab initio* calculations (B. Lange).

Inspired by the successful calculation of **finite-temperature *ab initio* thermodynamics** for bulk metals, we extended the method to **defects in oxides** within a visiting PhD student program financed by the Chinese Ministry of Education. A major challenge arises from long-range Coulomb interactions that render the direct approach of deriving the dynamical matrix from a series of force calculations impractical. Splitting the interatomic interactions into a long-range Coulomb part and short-range harmonic corrections restores the locality of the phonon model parameters. This locality makes the model amenable to parameterization from DFT and holds not only for ionic bulk materials, but even for charged defects. First results for the oxygen vacancy in MgO show that the presence of a defect modifies the effective charges of nearby atoms in a non-trivial way: as the

local symmetry is broken, the apparent charge becomes dependent on the direction in which the atom moves. The vacancy has dramatic consequences for the phonon density of adjacent shells, and hence the vibrational free energy derived from it. The contribution of zero-point vibrations to the free energy can be as large as 0.1 eV – a magnitude that one only would expect for the lightest of all atoms, i.e. hydrogen. The vibrational entropy is even enhanced upon vacancy formation – counter-intuitively, since in total, three degrees of freedoms are lost. These surprises highlight that the common assumptions on the (un) importance of vibrations for formation energies need be revised for defects (J. Wang).

On the **methodological side**, we were able to show in collaboration with Chris Van de Walle (University of California, Santa Barbara) that major discrepancies in calculated defect energies with traditional LDA/GGA functionals and more recent hybrid functional calculations can be largely resolved by the consequent application of charge corrections and realignment of the calculated band structure to deep charge transition levels [42]. Applying these techniques allowed us to understand the doping limiting mechanisms in optoelectronic materials and to revise the conventional doping picture by a new one that is consistent with recent experimental findings [43] (B. Lange). These activities are part of our collaboration with OSRAM.

The state of the art of defect calculations has now reached the point where it is high time to push forward their application to fields that previously seemed inaccessible due to the required accuracy of prediction. We have therefore organized in late 2011 a **workshop to bring together leading theoreticians from solid state theory and electrochemistry**. In a thriving atmosphere of inspired discussions, the participants shared their knowledge on a number of common key questions such as the inclusion of long-range electric fields due to charged defects, that are looked at very differently from each field's historical perspective.

The dangling-bond defect in hydrogenated amorphous silicon, that we study in the 5-year EPR Solar network project funded by the German ministry of research, is a prime example of a **defect in an amorphous/disordered system** (see p. 151). Our detailed analysis of the EPR parameters of this defect in comparison to dangling-bond-like defects in crystalline silicon has revealed how the specific characteristics are intimately linked to those of the amorphous matrix [44] and helped to interpret the experimental EPR spectra in terms of local structures. In contrast to previous work based on a rather idealized, textbook picture of a dangling bond, we show that the observed red-shift of hyperfine satellites results from an electronic delocalization, intrinsic to amorphous silicon, rather than a geometry-induced rehybridisation [45] (G. Pfanner).

To better understand the properties and growth of **ternary nitride alloys for optoelectronic device applications**, we study local ordering phenomena in epitaxially strained $\text{In}_x\text{Ga}_{1-x}\text{N}$ layers and the associated finite-temperature thermodynamics by means of Monte-Carlo simulations. The underlying empirical potentials were parameterized from DFT calculations and capture the relevant chemical and elastic interactions. Our results show a strong tendency for next-nearest neighbor ordering, culminating in ordered alloys at 33% and 66% In concentration, see Fig. 9. Alloys of intermediate concentrations can be understood in terms of patches of these ordered phases. It is currently investigated if this notion can be used to construct reliable continuum models with nanoscale composition fluctuations that can be parameterized from the ordered phases only (S. Lee).

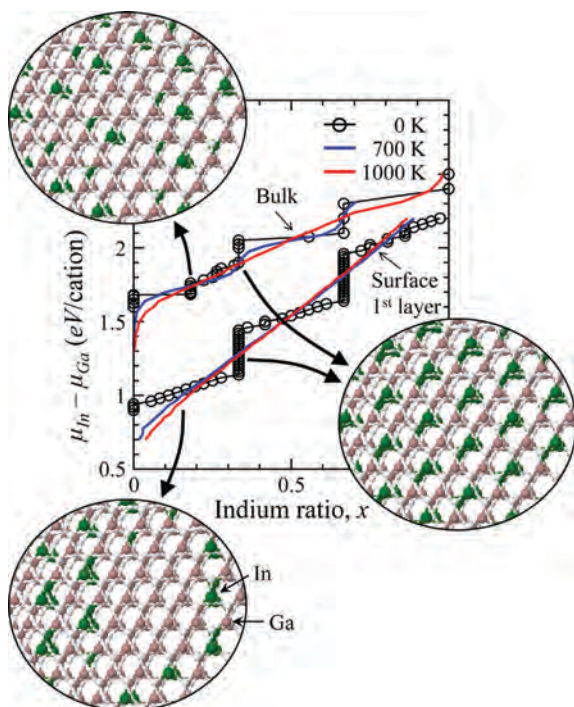


Fig. 9: Ordering phenomena and thermodynamics for wurtzite $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys, epitaxially constrained to GaN. The graph shows the chemical potential for a bulk material and a 3-layer thin film covered by an In adlayer. Insets highlight the corresponding ordered structure at 0 K. Thin films not only show a much higher tendency to incorporate indium, they can decompose laterally into ordered phases. This is enabled by vertical relaxation near the surface that is elastically suppressed in thicker films.

Adaptive Structural Materials (B. Grabowski)

The Adaptive Structural Materials (ASM) group established in April 2012 has a unique construction within MPIE: It is a hybrid theoretical-experimental group where an equal number of scientists from the CM and MA department work jointly together (see also *New Research Groups*, p. 13). The special task of the ASM group is to foster and further optimize the already intensive interdepartmental collaborations to a yet greater extent. To address the needs of such a mixed group, the theoretical unit of ASM has to cover

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a wide scope of computational techniques and methodological tools.

The backbone of ASM's applied research is closely related to the ERC SMARTMET project (see *Large Scaled Projects*, p. 25). The main aim is to boost next-generation **mechanical properties beyond present limits**. The key to this is a well-controlled application of intrinsic phase instabilities. Thus, an accurate and efficient determination of free energies, which determine stability regimes, is of central importance. The group has therefore strong ties to the group "Computational Phase Studies" (CPS, p. 38) and method development related to this topic is done in well-arranged collaborations. In these collaborations the ASM group has its main focus on the description of **instabilities and anharmonic contributions**. An example is the co-supervision of the project of D. Korbmayer (ASM) by A. Glensk (CPS) where previously developed *ab initio* methods [3] are extended to enable a highly accurate description of **temperature driven phase transitions** in Ti-alloys.

Another example is the co-supervision of the project of L. Xu (ASM) by F. Körmann (CPS) where the separately developed methods for describing anharmonicity and spin excitations are coupled. This will allow a much more **precise description of steels at high temperatures**. A backward flow of knowledge (ASM to CPS) is likewise established, for instance, by the input of ASM's expertise (B. Grabowski) into an accurate description of **point defects up to melting temperature** including all relevant finite temperature excitations (see p. 147) [22].

The **Gum Metal project** (see p. 113) is a first concrete application of the ideas behind SMARTMET. Specifically, Ti-Nb based alloys are considered which acquire special mechanical properties due to an extreme softness of their elastic constants. The work on Gum Metal is done in direct collaboration with the experimental part of the ASM group (C. Tasan, MA department). First achievements are related to revealing new plasticity mechanisms and to establishing the importance of oxygen. Future theoretical steps will be directed towards calculation of instability phase diagrams which are crucial in determining the Gum Metal effect (L. Huang).

Another attempt to overcome present mechanical limits is pursued within the **nano-pearlite project** (see p. 107). Nano-pearlite reaches the highest strengths ever achieved for a structural alloy, making it highly attractive to understand the underlying mechanisms. The project requires an intensive collaboration with experimentalists (Y.J. Li, MA department) and the development and application of a wide range of simulation tools. Important theoretical results include the *ab initio* based determination of the thermodynamic driving force for carbon redistribution [46]. Present investigations concentrate on the influence of dislocations where drag effects are simulated using the nudged elastic band method and

molecular dynamics employing empirical potentials (A. Nematollahi).

A third pillar of the ASM group is the **hydrogen enhanced local plasticity (HELP) project** aiming at understanding and eventually overcoming hydrogen embrittlement. Tackling the challenges related to H embrittlement is a tremendous effort requiring expertise from various fields. The project is therefore pursued in close collaboration with the "Mesoscale Simulations" and "Computational Phase Studies" group (both CM department). Additionally, a close link to the group R. Kirchheim from the University of Göttingen exists, which recently led to a joint DFG proposal application on this topic. The focus of the ASM group within the HELP project lies on extending the previously developed methodology [47] to iron based systems and to provide a validation of the empirical potential simulations with *ab initio* methods. To this end, the ASM group was recently joined by an expert in such calculations (G. Leyson).

To provide the necessary technical basis for the above projects, strong activities in method development are undertaken. The guiding principle can be summarized as **highest accuracy with minimum computational time**. The accuracy aspect is tackled at various length and time scales. At the smallest scale, the typically applied *ab initio* methods in form of density functional theory, which are limited by the approximation to describe exchange-correlation, are extended towards an even more fundamental approach, the **Quantum Monte Carlo approach**. In collaboration with M. Morales-Silva from the Lawrence Livermore National Lab the possibility of establishing a Gold Standard for *ab initio* simulations of metallic systems with Quantum Monte Carlo is investigated.

On the density-functional-theory level, the ASM group strives to further increase the accuracy/efficiency ratio in calculations of the computationally demanding **anharmonic contributions** important for phase stability (D. Korbmayer, L. Huang). On the empirical potential level, efforts are undertaken to increase the accuracy of presently available **embedded atom potentials** (M. Grabowski).

In its development, the ASM group significantly profited from projects (e.g., nano-pearlite and HELP) that were inherited from a former group of the CM department (Microstructure, J. von Pezold). A special highlight that grew up in the former group and is now successfully hosted in the ASM group provides new and exciting insights about grain boundary motion (C. Race, see p. 121). These projects quickly got ASM under way. Two new projects will start within the next few months. O. Vekilova will contribute her expertise in calculating ***ab initio* elastic constants at finite temperatures** to ASM's efforts related to the SMARTMET project. L. Huber will join from a group specialized in multiscale modeling of microstructure evolution (M. Militzer, University of British Columbia). He will work within a DAAD research fellowship on the **influence of solutes on grain boundaries in iron**.

Mesoscale Simulations (R. Spatschek)

The research in the group is devoted to the understanding of **phenomena appearing on dimensions between the atomic and continuum scales**. As a generic feature the microstructure of a material intrinsically links these scales, thus naturally connecting to the other groups within the department and institute. Various computational and analytical techniques, which are particularly tailored to the different applications, are used in the group. The further development and improvement of models and simulation techniques is also an important activity. In the following, recent key activities in the group are briefly discussed.

A fascinating research area, which has attracted intense interest during the past years is related to **grain boundary premelting**. Here, depending on the type of the grain boundary and the local misorientation, a melt film can form along the grain boundary already below the bulk melting point. It therefore has tremendous influence on the stability of materials at elevated temperatures and affects dendrite coalescence and microstructure evolution. Understanding this phenomenon demands to link mesoscale thermodynamic concepts to atomic scale elastic distortions due to the presence of misfit. We used phase field crystal and Ginzburg-Landau techniques, which are related to classical density functional theory, to predict this material failure mechanism. We shed light on the role of the underlying short range structural disjoining forces, also in conjunction with thermal noise. In particular, we were able to extract the asymptotic behavior of the disjoining potential, leading to a fully analytical prediction of the gamma surfaces close to the melting point. Presently, we link these findings to the kinetics of **liquid metal embrittlement**, which is a major problem e.g. for welding of zinc coated steels. Here, we model the melt invasion along a grain boundary taking into account the aforementioned structural forces, in combination with aspects of crack propagation [48-51] (C. Hüter, F. Twiste).

Further activities are related to the field of **heterogeneous nucleation and microstructure evolution**, embedded into the DFG priority program 1296. Our aim is to understand the role of elastic effects both on the initial regime of nucleation as well as the long time evolution of microstructures. Recent activities are related to the growth of **nanowires**. Here we studied in particular the competing elastic and interfacial effects, which limit the aspect ratio of the forming nanowire. Also, we investigated so called pine tree nanowires, which are grown around a screw dislocation in their center and generating a twist of the wire around this axis. The arising internal elastic stresses destabilize the wire and favor the Rayleigh-Plateau decomposition into droplets [52,53] (G. Boussinot, R. Schulz).

We studied **solidification** of monotectic and syntectic alloys, which are relevant for lead-free soldering. The common feature of both systems is the appearance of phase separation in the melt phase, allowing for phase coexistence of two liquid and one solid phase. The steady state growth has been analyzed theoretically using Green's function methods and phase field techniques (see Fig. 10). The outcome of these studies is the prediction of the growth velocity and length scales of the emerging microstructures, depending on the undercooling and alloy composition [54] (G. Boussinot, C. Hüter).

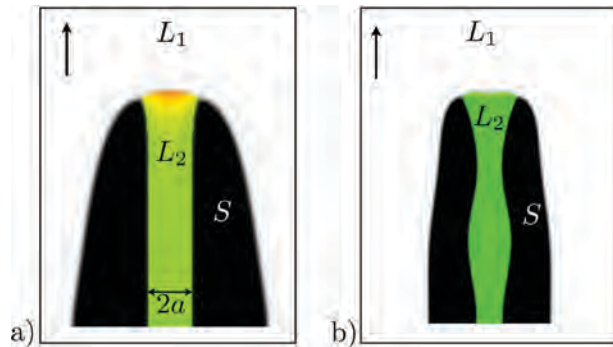


Fig. 10: Solidification of a monotectic alloy. Two-phase finger with the solid (black) surrounding the liquid L₂ (green/grey) in a) steady state, b) oscillatory regime. The arrow indicates the growth direction.

The Ginzburg-Landau methods, which link atomistic modeling to large scale mesoscale phase field simulations, have also been used to study grain boundaries in bcc δ -iron near the melting point. In agreement with phase field crystal and molecular dynamics simulations we find a transition between a state of paired edge dislocations and a splitting into individual dislocations with a mixed edge end screw character at lower temperatures (see Fig. 11). This **dislocation pairing transition** is an important benchmark for the rather recently developed Ginzburg-Landau model in our group. The underlying codes, which have been developed in our group, are run efficiently on GPUs, with an acceleration up to a factor 250 in comparison to a single core CPU code [55] (C. Hüter).

Another important reason for material failure in high-strength steels is **hydrogen embrittlement**. Our focus here is on hydride forming materials, which nucleate a hydrogen-saturated region in particular near defects like edge dislocations and therefore favor a ductile-to-brittle transition. As a prototype we simulated the Ni-H system using Monte-Carlo simulations and molecular statics. The full quantitative linking to a macroscopic and thermodynamic description, taking into account nonlinear elastic effects opens the path for a true and quantitative scale bridging modeling of material failure. The elaborated free energy model can directly be used e.g. in phase field models and is presently used to predict the stress induced hydride



formation at crack tips. This project is part of the DFG Collaborative Research Center 761 “Steel *ab initio*” [9] (D. Korbmacher, J. v. Pezold, C. Hüter).

A more methodological development is pursued in the coupling of **phase field models with plasticity**. In many transformations in steels stresses reach rather high values such that plastic deformations are involved. We have worked out a general framework that couples these two aspects, focusing on the issue of internal variables describing the plastic state. It turns out that the evolution equations for front propagation do not follow uniquely from variational principles [56].

Phase change materials are exciting candidates for fast and nonvolatile data storage. The basic concept is a phase transformation between an amorphous and a crystalline state, triggered by the heat generated by an electrical current. The different conductivities between the phases allow to distinguish between the phases and thus to store information in the memory cell. In this project we focus on the kinetics of the switching process, and we developed a phase field model to simulate the Joule heating induced phase front propagation. In order to overcome the high computational cost of these simulations, a GPGPU implementation has been implemented, leading to a code acceleration by two orders of magnitude in comparison to a conventional CPU code. This activity is linked to the DFG Collaborative Research Center 917 “Nanoswitches” [57,58] (G. Boussinot, A. Monas).

Other Activities

Corrosion, Surface and Interface Related Activities (M. Todorova)

Processes occurring at surfaces or interfaces of materials can influence their properties in a multitude of different ways. Examples are embrittlement, corrosion or catalytic reactions, which might be desired or not, depending on a targeted functionality. Various activities have been initiated and supervised by M. Todorova:

In the manufacturing of high quality steel products, processing steps and costs can be reduced by hot-forming of already coated steel plates. Such a process has been observed to lead to degradation of the quality of work pieces, caused by **liquid metal embrittlement** of bulk steel coming into contact with liquid zinc. The mechanisms underlying this process were investigated in the diploma work of K.-D. Bauer in a collaborative effort involving the Zentrum für Oberflächen und Nanoanalytik, Johannes Kepler University Linz (K. Hingerl). Combining DFT with a modified Griffith model we were able to explain the liquid metal embrittlement in the hot-forming process of galvanised steel: Zinc

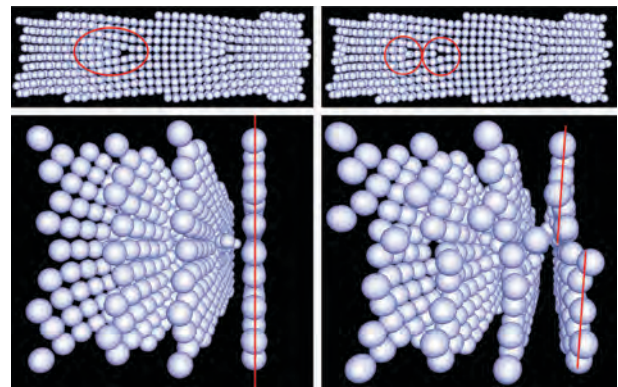


Fig. 11: Symmetric tilt in bcc δ -iron. At high homologous temperatures of more than about 85% of the melting temperature the dislocations have a pure edge character (left panel). For lower temperatures they split into partials with additional screw character, leading to out-of-plane deformations. Top row: View onto the grain boundary. Bottom row: View along the grain boundary.

is found to wet grain boundaries and to promote fracture along them, by significantly reducing the costs for crack propagation – even a single monolayer of zinc decreases crack propagation cost in a $\Sigma 3$ grain boundary by 22% and in a (more realistic and suggested by experiment) $\Sigma 5$ grain boundary by 43% (K.-D. Bauer).

Stoichiometric **iron aluminides** are candidate materials for high temperature applications, but their applicability is impeded by a poor room temperature ductility caused by **environment-induced embrittlement**. It has been suggested in the literature that both addition of suitable alloying elements, as well as the presence of passive surface films may reduce the problems caused by hydrogen. Aiming to understand the effects either of these processes may have, we focus on Fe_3Al . On one hand we investigate the preferential surface terminations of the clean surfaces and their interactions with oxidising species, which will allow us to identify changes in the surface behaviour upon addition of alloying elements. On the other hand, we look into both the coupling to the substrate and the stabilisation subject to the environmental conditions (employing surface phase diagrams) of passivating Al_2O_3 (A. Izanlou).

Magnesium is one of the lightest metals with potential applications ranging from automotive, to aerospace to medical applications. Understanding the **corrosion behaviour of Mg and its alloys**, when in contact with an oxidising environment is important for any of these (applications) and serves as important model system for other materials. Performing DFT calculations for Mg in contact with different oxidising species (N, O, F and Cl) allowed us to address the propensity of Mg to oxidise and identify similarities and differences in its behaviour towards the different oxidising agents (S.-T. Cheng).

Corrosion in sour gas media is a particular problem for low-alloyed steels. Iron-sulphide layers which form under the influence of the sour gas environment have been observed to sometimes have a beneficial effect by providing a diffusion barrier for further penetration of harmful species. Morphology and stability of the capping layer are hereby of central importance. We aim to gain a deeper insight into the interactions, which lead to the formation of **Fe-S layers at the surface**, address their composition and structure, and understand the mechanisms and conditions which influence their passivating function. The gained insight is expected to aid systematic improvement of the corrosion properties of low-alloyed steels in sour gas media (M. Ilhan, to start on 1 Jan. 2013).

Epitaxy and Surface Characterization (L. Lymperakis)

Group III-Nitrides and their ternary alloys are materials of choice for high temperature and high power microelectronic devices which are of special interest for the automobile industry as well as for solid state lighting (SSL) and chemical and biological sensor applications. L. Lymperakis is involved in two EU funded projects: (i) The Industry-Academia Marie-Curie project SINOPLE and (ii) the Nanosciences, Nanotechnologies, Materials and new Production Technologies project ALIGHT. Topics that are addressed in this area are:

The growth of high In content as needed to access the green region of the spectrum and high quality InGaN films is challenging: The size difference between In and Ga as well as the difference in In-N and Ga-N bond strengths has been suggested to result in In surface segregation, limited In incorporation as well as **spinodal decomposition and phase separation**. To overcome these obstacles low growth temperatures are commonly used that however result in rough surface morphologies and impaired crystal quality. Using *ab initio* techniques, we have **computed surface growth diagrams** showing the most stable structures as function of the growth conditions. These calculations naturally include **surface segregation** effects and allow to identify optimum growth conditions (A. Duff).

High resolution transmission electron microscopy (HRTEM) imaging combined with a subsequent strain analysis allows to **map the HRTEM measured lattice parameter into a local chemical composition**. Conventional approaches, however, assume for the underlying analysis a homogeneous and linear elastic medium. Since in actual HRTEM very small volumes are probed, atomic scale effects may become important. We have therefore combined large scale modified embedded atom method (MEAM) calculations with HRTEM experiments and image simulations on ternary $\text{In}_x\text{Ga}_{1-x}\text{N}$ Quantum Wells (QW) embedded

in a GaN matrix. Our approach revealed that these alloys are structurally inhomogeneous on the atomic scale and exhibit strong interactions between adjacent cells. Both effects may result in misinterpretation of the HRTEM images such as erroneous chemical clustering (A. Duff, in cooperation with M. Albrecht, Leibniz Institute for Crystal Growth, Berlin).

Scanning tunneling microscopy (STM) is commonly believed to offer an **exceptional sensitivity to surface states** combined with unprecedented atomic resolution and constitutes one of the most appropriate methods to probe the surface atomic and electronic structure. Addressing an on-going controversial debate regarding the electronic structure of non-polar GaN surfaces we could demonstrate that under certain conditions surface states may be fully shadowed by bulk states and invisible in normal STM operation modes. Based on this insight and using the *ab initio* computed bandstructure we designed a new STM operation mode that our experimental partners successfully used to probe and identify hidden surface states (in cooperation with Ph. Ebert, Peter Grünberg Institut, FZ Jülich GmbH).

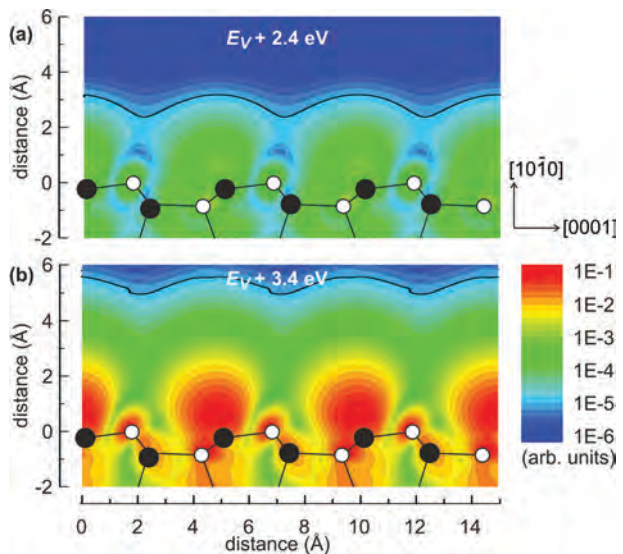


Fig. 12: Spatially resolved density of states as seen by an STM at two different tunnel voltages for the example of a GaN (1100) surface. The fast decay of the surface states into vacuum is clearly seen and results in low (bulk like) corrugation at typical surface-tip distances (black line).

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Research Projects in Progress

Computational Phase Studies

Dutta, Hickel, Neugebauer (in collaboration with K.R.A. Ziebeck, K.U. Neumann*, P. Entel** (*Loughborough University, UK, **Univ. Duisburg-Essen)): Ab initio investigation of temperature dependent effects in shape memory Heusler alloys*

Dutta, Hickel (in collaboration with A. Hütten, I. Opahle**, G. Madsen**, R. Drautz**, A. Waske*** (*Universität Bielefeld, **Ruhr-Universität Bochum, ***IFW Dresden)): Ab initio study on the coupling of lattice and magnetic degrees of freedom and the role of interfaces in magneto-caloric materials*

Aydin, Hickel, Neugebauer (in collaboration with R. Drautz, ICAMS Bochum): Chemical trends for the solubility and diffusion of hydrogen in metals with high-throughput calculations

Bleskov, Hickel, Neugebauer, Raabe (in collaboration with R. Dronskowski, B. Hallstedt et al., RWTH Aachen): Ab initio calculation of free energies, stacking-fault and grain-boundary energies at finite temperatures in Fe-Mn-C alloys

Körmann, Hickel, Nematollahi, Grabowski, Neugebauer (in collaboration with S.V. Okatov, Yu.N. Gornostyrev*, A. Leineweber** (*Ekaterinburg, Russia, **MPI Stuttgart)): Formation of Fe₃C precipitates in ferritic steels*

Glensk, Grabowski, Hickel, Neugebauer (in collaboration with B. Hallstedt, I. Egrý**, R. Schmid-Fetzer***, M. Rettenmayr**** (*RWTH Aachen, **DLR Köln, ***TU Clausthal, ****U Jena)): Ab initio determination of Helmholtz free energies and derived properties (phase diagrams, heat capacities, thermal expansions) for Al alloys containing Si, Mg and Cu*

Körmann, Hickel, Neugebauer (in collaboration with M. Palumbo, S. Fries*, B. Hallstedt** (*ICAMS,*

*Bochum, **RWTH Aachen)): Ab initio simulation of magnetic contributions to the thermodynamics of metals,*

Nazarov, Hickel, Neugebauer (in collaboration with L. Duprez, R.G. Thiessen**, K. Mraczek***, H. Hänninen****, Y. Yagodzinskyy**** (*OCAS, Belgium, **TKS, Duisburg, ***VoestAlpine, Austria, ****Aalto Uni, Finland)): Hydrogen sensitivity of different advanced high strength microstructures*

Hickel, Neugebauer (in collaboration with Y. Ouyang (Guangxi University, China)): Mechanisms of self and impurity diffusion in Fe-Al intermetallic compounds

Dey, Nazarov, Hickel (in collaboration with D. Mirkovic, T. Evertz, F. Klose, Salzgitter Mannesmann Forschung GmbH): Investigation of hydrogen and carbides in HSD steels

Zhang, Hickel, Neugebauer (in collaboration with J. Rogal and R. Drautz, Ruhr-Universität Bochum): The role of interfaces for the martensite formation in steels

Körmann, Grabowski, Hickel (in collaboration with S. Fries, Ruhr-Universität Bochum): Sapiens – Thermodynamic modeling of unary metals

Hickel, Friák, Neugebauer (in collaboration with Y. Gornostyrev, CJSC Institute of Quantum Materials Science, Ekatarinburg): Ab initio prediction of thermodynamics and kinetics of clustering in maraging steels

Hickel, Körmann (in collaboration with E. Povoden-Karadeniz, Institute of Materials Science and Technology, Vienna): Thermodynamic modeling of TCP phases

Körmann, Hickel, Neugebauer (in collaboration with Z.-K. Liu, Pennsylvania State University): Modeling of paramagnetic properties of metals



Ab Initio Thermodynamics

Friák, Neugebauer (in collaboration with G. Brückner, H.H. Angermann**, B. Sahebkar***, B. Kuhn****, H. Hattendorf*****, S. Weber***** (*ThyssenKrupp Nirosta GmbH, **Behr GmbH & Co. KG, ***Benteler Automobiltechnik GmbH, ****Forschungszentrum Jülich, *****ThyssenKrupp VDM GmbH, *****Ruhr-Universität Bochum)):* Development of ferritic steels for high-temperature applications („Ferrit950“)

Friák, Neugebauer (in collaboration with J. Eckert, H. Emmerich** (*Leibnitz-Institut für Festkörper- und Werkstofforschung Dresden, **Universität Bayreuth)):* Scale bridging studies of the elastic contributions to nucleation and initial microstructure formation in the eutectic system Ti-Fe

Friák, Neugebauer (in collaboration with A. Ziegler (Universität Ulm) and S. Hild (Johannes Kepler Universität Linz)): Ab initio and atomistic calculation of thermodynamic and mechanical properties of biomaterials

Friák (in collaboration with M. Šob, Brno): Ab initio calculations of phase transformations in iron

Friák (in collaboration with A. Dlouhý, D. Holec** (*Academy of Sciences of the Czech Republic, **Universität Leoben)):* Ab initio calculations of phase transformations in NiTi

Friák (in collaboration with M. Zelený, Uppsala University): Ab initio studies of martensitic phase transformations

Friák (in collaboration with P.H. Mayrhofer, D. Holec, Universität Leoben): Ab initio study of hard nitrides

Friák (in collaboration with M. Šob, Academy of Sciences of the Czech Republic): Ab initio investigation of Ni-N compounds

Defect Chemistry and Spectroscopy

Freysoldt, Pfanner, Neugebauer (in collaboration with F. Finger, K. Lips**, A. Schnegg**, R. Bittl***, M. Brandt**** (*Research Center Jülich, **Helmholtz-Zentrum Berlin für Materialien und Energie, ***FU Berlin, ****TU München)):* EPR-Solar – Ultra-high resolution EPR spectroscopy on thin film silicon for solar cell research

Freysoldt, Neugebauer: Accurate calculation of the electronic structure at grain boundaries via density functional theory and quasi particle corrections

Freysoldt (in collaboration with S. Boeck, K. Reuter** (*Gemmanetics IT Consulting, Erkrath, **GRZ Garching)):* SPHInX parallelization

Cui, Freysoldt, Neugebauer (in collaboration with OSRAM Opto Semiconductors GmbH): Non-radiative recombination at point defects in III-nitrides

Lee, Freysoldt, Neugebauer: Ordering effects in epitaxial InGaN alloys

Lange, Freysoldt, Neugebauer: Energy decomposition based on Quamols

Lymperakis, Freysoldt (in collaboration with National University of Ireland, Universität Ulm, University of Cambridge, and Osram Opto Semiconductors GmbH): ALIGHT: AlGaInN materials on semi-polar templates for yellow emission in solid state lighting applications.

Lymperakis (in collaboration with Forschungsverbund Berlin e.V. and Topgan Ltd., Warschau): SINOPL: Surface engineered InGaN heterostructures on N-polar and non-polar GaN-substrates for green light emitters

Adaptive Structural Materials

Grabowski, Neugebauer (in collaboration with C. Tasan and D. Raabe, MA department): SMART-MET: Adaptive nanostructures in next generation metallic materials

Grabowski, Neugebauer (in collaboration with M. Morales-Silva, Lawrence Livermore National Lab, USA): Towards a golden standard for first principles calculations in metallic systems

Grabowski, Glensk, Hickel, Neugebauer: Ab initio simulations of point defects up to melting: Reconciling theory and experiment

Grabowski, M., Grabowski, B., Neugebauer: Improving accuracy of present day's empirical potentials

Huang, Grabowski, Neugebauer (in collaboration with C. Tasan, D. Ma, S. Sandlöbes, H. Springer, D. Raabe, MA department): Theoretical-experimental investigation of Gum metal plasticity

Korbmayer, Grabowski, Glensk, Neugebauer: Highly accurate description of temperature driven phase transitions in Ti-alloys

Lei, Grabowski, Körmann, Neugebauer: Integrated coupling of anharmonic and magnetic excitations

Leyson, Grabowski, Hickel, Neugebauer (in collaboration with R. Kirchheim, University Göttingen): Investigations and calculations of the interaction of hydrogen with dislocations in iron and nickel

Nematollahi, Grabowski, Neugebauer (in collaboration with Y. Li, MA department): Atomic scale analysis of the origin of pearlite's strength

Race, Neugebauer: Understanding grain boundary migration



Mesoscale Simulations

Chakrabarty, v. Pezold, Hickel, Spatschek, Neugebauer: Ab initio based description of hydrogen embrittlement

Spatschek (in collaboration with H. Müller-Krumbhaar, Research Center Jülich): Elastic effects on heterogeneous nucleation and microstructure evolution

Spatschek (in collaboration with A. Karma, North-eastern University): Grain boundary premelting

Spatschek (in collaboration with H. Löwen, Heinrich-Heine-Universität Düsseldorf): Liquid metal embrittlement and wetting of grain boundaries

Spatschek (in collaboration with I. Steinbach, Ruhr-Universität Bochum): Hydrogen at crack tips

Spatschek (in collaboration with S. Brinckmann, Ruhr-Universität Bochum): Dual scale modeling of hydrogen embrittlement

Spatschek (in collaboration with I. Steinbach, Ruhr-Universität Bochum): Pine tree nanowires

Spatschek (in collaboration with B. Eidel, Universität Essen): Phase field modeling with plastic effects

Spatschek (in collaboration with E. Brener and M. Apel** (*Research Center Jülich, **ACCESS Aachen)): Modeling of phase change materials for nonvolatile data storage*

Spatschek (in collaboration with E. Brener, Research Center Jülich): Pattern formation during solidification and melting

Corrosion

Cheng, Todorova, Friák, Neugebauer (in collaboration with M. Rohwerder, GO department): Ab-initio investigation of the corrosion behaviour of magnesium and its alloys

Izanlou, Todorova, Friák, Neugebauer (in collaboration with M. Palm, SN department): Theory-guided materials design of Fe-Al alloys resistant to environment induced brittleness

Nykaenen, Todorova (in collaboration with R. Schlögl, MPI Mülheim): Platinum surfaces in contact with water

Todorova (in collaboration with M. Tröger, Salzgitter Mannesmann Forschung GmbH): Characterization of iron-sulphide layers

Todorova (in collaboration with K.-D. Bauer and K. Hingerl, Zentrum für Oberflächen und Nanoanalytik, Johannes Kepler University Linz): Modeling liquid metal embrittlement

*Vatti, Todorova (in collaboration with M. Valtiner, GO department): Direct experimental measurement and theoretical *ab initio* simulations of hydration layers and specific ion adsorption at confined solid/water/solid interfaces*



Department of Interface Chemistry and Surface Engineering

M. Stratmann

Introduction and Retrospective

The Department of Interface Chemistry and Surface Engineering (GO department) is conducting fundamental research in the electrochemical sciences, with a strong **focus on corrosion and adhesion science as well as electrochemical energy conversion**. Our mission is to combine both fundamental and applied sciences to tackle key-questions for a progress towards new or better, energy saving and efficient, cheaper and longer lasting materials for applications in structural (in particular steels and other alloys) and functional materials, e.g., for fuel cell catalysts, batteries, adhesives, coatings, nano-porous metallic glasses among others. The department hosts six research groups and the Christian-Doppler-Laboratory (CDL) for Diffusion and Segregation during Production of High Strength Steel Sheet (Dr. M. Rohwerder), which was established in 2008. The different groups focus on high-throughput methods and development of combinatorial methods in adhesion science and electrochemistry, as well as characterization of electrified interfaces by complementary methods such as vibrational spectroscopy, *in-situ* diffraction studies and scanning probe techniques, including Scanning Kelvin Probe (SKP), Atomic Force Microscopy (AFM) or Scanning Tunneling Microscopy (STM). We combine electrochemistry with a surface and interface science approach, and in most projects we complement both, atomically well-defined experi-

mental studies and experiments with real systems by atomistic *ab initio* and larger-scale (continuum theory) modelling. **All groups in the department have their independent and strong research agenda, while collaborative research projects are synergistic and focus on major challenges** and complex scientific questions that require the scale and interdisciplinarity (detailed below).

In the last 6 years the group structure of the department was subject to a number of advancements and adjustments: In 2007, Prof. G. Grundmeier (head of the former Thin Films Group) was appointed full professor and chair of the Department for Technical and Macromolecular Chemistry at the University of Paderborn (UPB, Germany). Also in 2007, Dr. M. Spiegel (head of the former high-temperature corrosion group) changed to the R&D department of Salzgitter-Mannesmann. As a consequence, two new groups, the Interface Spectroscopy (Dr. A. Erbe), and the Interface Structures and High Temperature Reactions (Dr. F.U. Renner) groups were established in 2007. In 2009, Prof. A.W. Hassel (head of the former Electrochemistry group) was appointed full professor and chair of the Institute for Chemical Technology of Inorganic Materials at the University of Linz (Austria). Accordingly, a new group in the field of Electrocatalysis (Dr. K.J.J. Mayrhofer) could be established. In 2010 the CDL-Laboratory for Polymer/

Research Groups	Scientific Interests	Laboratories
<ul style="list-style-type: none">• Atomistic Modeling• Electrocatalysis• Interaction Forces & Functional Materials• Interface Spectroscopy• Interface Structures & High Temperature Reactions• Molecular Structures and Surface Design• CDL for Diffusion and Segregation During Production of High Strength Steel Sheets	<ul style="list-style-type: none">• Electrochemical Sciences• Corrosion• Adhesion, Thin Films and Friction• Functional Surfaces and Interfaces• Industrial Processes• Fundamental Research and Simulation	<ul style="list-style-type: none">• Adhesion Science and Tribology• Chemical Analysis• Clean Room• Co-deposition (PVD, CVD, PLD)• Corrosion Testing• μ-Electrochemistry• Kelvin Probes• High-Resolution SAM/ SEM/ EDX/ EBSD• Optical Spectroscopy• Scanning Probe Techniques• X-ray Diffraction• Surface Science (XPS, SIMS)

Fig.1: Research groups, scientific interests and laboratories at the Department of Interface Chemistry and Surface Engineering.

Metal Interfaces (managed by Prof. G. Grundmeier, UPB) was concluded after 7 successful years.

In the last two years the department had **two further changes of the senior academic staff**. Dr. A.A. Auer (atomistic modelling group) left the institute in February 2012, to establish a modelling group at the Max-Planck-Institute for Energy Conversion in Mülheim. His newly established team collaborates closely with our department in many research projects, such as the correlation of experiment and simulation of adhesion and stability of Pt-nanoparticles on carbon supports and the oxygen reduction mechanism (see p. 129). With the **newly established group in the field of "Interaction Forces and Functional Materials"** (Dr. M. Valtiner) novel experimental setups and laboratories (Surface Force Apparatus and Interaction Forces Laboratory, see p. 16) and competences in particular in the fields of adhesion, friction and bio-functionalization at electrified materials interfaces complement the existing portfolio of the department. As a winner of a BMBF grant (Dr. K.J.J. Mayrhofer), the newly established laboratory for "Differential electrochemical mass spectrometry and gas chromatography" is focused on electrochemical energy conversion and electrochemical reduction of CO₂ (see p. 18).

Over the last six years our **efforts in fundamental and complementary industrial research have established a dynamic department with a unique research portfolio and expertise** (see Fig. 1). The department is also actively participating in various collaborative research efforts with internal and external partners. Several scientists of the department are participating in the DFG Cluster of Excellence "Ruhr Explores Solvation" (Resolv), which is centred at Ruhr University Bochum's (RUB) Faculty of Chemistry and Biochemistry. Resolv was awarded in the latest round of the excellence initiative, and commences operation on 1 November 2012. Our contributions to solvation science in Resolv will focus on the role of solvents in electrochemical reactions, and solvation of interfaces (see p. 27). Further, the department is part of a recently awarded EU 7th framework programme Marie Curie Initial Training Network (ITN) under the name of "Somatai - Soft Matter at Aqueous Interfaces". Somatai starts to become

reality on 1 October. The Center for Electrochemical Sciences (CES) was founded in collaboration with the RUB in 2009. CES is recognized as a Center of Excellence with the task to ensure international competitive research in all aspects of modern electrochemistry, covering both experimental and theoretical electrochemistry (for details see p. 22).

With its versatile experimental and theoretical expertise (also Fig. 1) the GO department is in the **unique position to assist and promote diverse industrial research areas by the understanding of their underlying fundamental electrochemical reaction mechanisms and kinetics**. For instance, electrochemical oxygen reduction reaction (ORR) - a key process in corrosion as well as energy conversion - has been the focus of several joint research projects in the GO department aiming at a fundamental understanding of its mechanism for better control in corrosion protection as well as improved catalysis in fuel cells and air batteries. These research projects combine both advanced electrochemical as well as *in situ* and *in operando* spectroscopic experiments with theoretical modelling.

The fundamental studies complement the second central focus of our department; the study of electrochemical processes that are of ultimate practical importance in industrial applications. Several research projects focus around phosphating and oxide thin-film growth and properties on engineering metals. Further, considerable research effort is centred on diffusion and segregation during production of high strength steel sheets, including e.g. the complementary experimental and theoretical investigations of grain-boundary oxidation processes. The effect of hydrogen in steel, a collaborative interest of the institute, has been investigated by complementary experimental and theoretical methods, and in particular the Scanning Kelvin Probe was further extended to uniquely and directly detect hydrogen in steel with high spatial resolution. The newly developed **Scanning Flow Cell (SFC) coupled to the inductively coupled plasma mass spectrometer (ICP-MS)** allows high-throughput screening of electro-catalysts or corrosion reactions combined with a simultaneous quantification of reaction products.

Scientific Concepts and Broader Impact

All our research groups are synergistically working on common areas of interest and we are strongly dedicated to collaborative work with external partners. Our scientific concept comprises diverse fundamental and industrial fields:

Electrochemical sciences

In the recent years extensive collaborative experimental and theoretical work focussed on the

electrochemical oxygen reduction reaction (ORR), a fundamental electrochemical reaction relevant in both corrosion as well as energy conversion processes. At metal surfaces the ORR is the cathodic partial reaction driving many corrosion processes. On the other hand, the electrocatalysis of the ORR in fuel cells and air batteries is intensely studied with the aim of improving the kinetics and reducing the overpotential that limits the energy efficiency.



Several cooperative research projects in the GO-Department have focussed on shedding light on the complex multi-step reaction mechanism that strongly varies with the electrocatalytic surface and reaction conditions. H_2O_2 , a known side product or intermediate, offers the opportunity to selectively study the serial pathway, which was exploited in combined electrochemical and theoretical investigations [1,2]. The H_2O_2 decomposition reactions on platinum were shown to be very fast (diffusion limited) for a wide range of potentials showing that the serial ORR pathway is possible even if H_2O_2 cannot be detected. Electronic structure calculations of the activation energies confirmed, that reaction pathways and kinetics of the peroxide decomposition are controlled by the oxidation state of Pt surfaces (see p. 129). Surface sensitive vibrational spectroscopy allows direct detection of ORR intermediates and thereby validation of the mechanism. A spectro-electrochemical ATR-IR setup has been developed and in a first application ORR on the model semiconductor surface $n\text{-Ge}(100)$ has been studied [3].

Within the last years, **the newly developed and unique Scanning Flow Cell (SFC) coupled to the inductively coupled plasma mass spectrometer (ICP-MS) depicted in Fig. 2** has become a workhorse for high-throughput investigations of the stability of electrocatalysts, and the study of electrochemical processes such as corrosion or dealloying [4-6]. This has been utilized to increase the **understanding of the (electro-)chemical dissolution of metals** as a critical process for both, the design and synthesis of new catalysts and the prevention of their degradation during operation. Due to the wide parameter-space for material composition and structure as well as operation conditions fast screening techniques are necessary to obtain reliable information within a reasonable timeframe. For this purpose the scanning flow cell (SFC) automated high-throughput technique has been extended to enable the analysis of finely dispersed, porous catalyst materials. In cooperation with the industry partners the activity and stability of different catalysts for the application in polymer electrolyte membrane fuel cells has been a central aspect of the SFC work. Polymer electrolyte fuel cell technology is considered as one of the possible alternatives for electromobility applications, however the extensive use of and the degradation of Pt especially at the cathode still prevents its commercialization. Alloying with transition metals is a common strategy to generate highly active yet stable ORR electrocatalyst, as it lowers Pt loadings and also increases the activity due to ligand or strain effects. However, the instability arising from the electrochemical dissolution of the less noble metal, causing a decrease in the activity and poisoning of the membrane remains. On the other hand, dealloying before implementation in

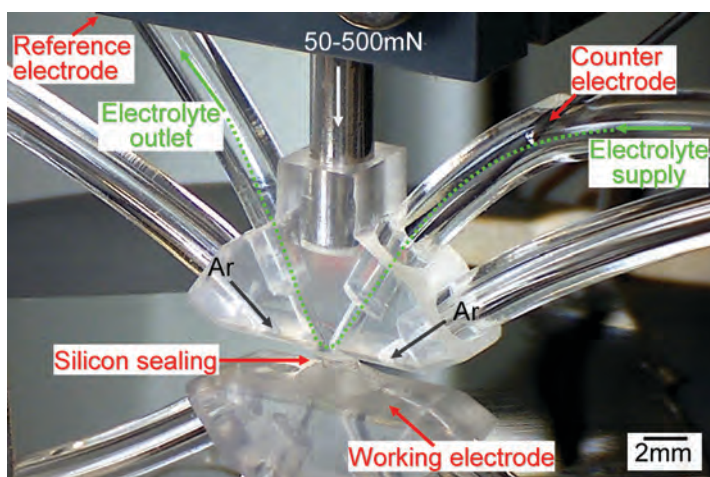


Fig 2: The core of the Scanning Flow Cell is an electrochemical cell made out of polyacryl with two channels for the electrolyte inlet and outlet that are housing the reference and counter electrode. The electrolyte flow is induced by a peristaltic pump (not shown). The cell has an opening at the bottom of 200-1000 μm surrounded by a silicone sealing, which defines the contact area on the working electrode sample. The electrolyte can be purged by various inert or reactive gases; additional gas line for creating an inert atmosphere around the sealing prevents oxygen diffusion through the silicone. The whole cell is mounted on a xyz-translational stage for automatic position control, and can be operated in a free hanging mode or full contact mode with controlled contact pressure.

the membrane-electrode-assembly can be a useful tool in designing catalysts as it improves activity compared to conventional catalysts [7]. To follow the microstructural changes of Pt-based catalysts at a nanoscale level we employ the combination of conventional electrochemical techniques and the Identical Location TEM approach (IL-TEM – see p. 131). The latter provides insights in the dealloying pathways, size dependent morphological changes and degradation process. Extending the IL-TEM to more sophisticated characterization techniques (HAADF-STEM, EELS and tomography) allows an investigation also of the compositional variation on the sub-nanometer scale and the development of a 3D reconstruction of the particle dispersion. Combining this approach with conventional electrochemistry provides a complete description of the catalytic activity in relation with the surface structural characteristics. The scientific aim is to understand the mechanisms that govern the corrosion of the materials in order to design catalysts with high stability without compromising activity. The SFC was complementarily used to characterize the **early stage of de-alloying of model Cu_3Au and Cu_3Pt single crystals** for developing a fundamental understanding of dealloying processes. To keep in touch with real world applications, high-surface-area bimetallic nanoparticles like CuPt were studied in parallel. Selective leaching of less noble elements from such nanosystems results in formation of porous and/or core/shell structures preserving the increased activity towards such important reactions as electrochemical oxygen reduction.

Currently, **Li-ion batteries** are the main alternative in use as energy storage in the automotive industry and in portable consumer electronics. The anode in Li-ion batteries represents a very reactive electrode, which often requires *in-situ* measurements to address the actual mechanisms at work during charging and discharging reactions. For the use with ionic liquids we have recently adapted and now intensively tested a UHV-compatible *in-situ* electrochemical X-ray diffraction chamber employed at synchrotron light sources. By their low interaction with matter especially high-energy photons in the range above 60 keV offer great possibilities for *in-situ* diffraction studies. Eventually replacing carbonaceous materials, silicon may become one of the most important anode materials in the future. Theoretically it can store many times more Li but structural and primarily volume changes pose currently still technical problems. Au nanoparticles are one way to obtain Si nanowires but the strong Au–Li signals obscure the interpretation of X-ray diffraction data from the Si nanowires. Here we started to examine pure Au model systems [8,9] with high-energy synchrotron light at the new light source PETRA3 in Hamburg and could unambiguously identify two metastable Au-Li phases, which constitute the main phases during cycling. Further work will focus on different Si-based materials and using the new **Pulsed Laser Deposition** system for producing thin film model electrodes.

Corrosion

The corrosion research of the department includes aqueous, atmospheric and bio-corrosion processes and their inhibition, covering both fundamental and applied aspects. In aqueous environments the SFC system with downstream analytics allows **electrochemical high-throughput screening and characterization of corrosion properties of material samples**. The setup allows the time-efficient investigation of samples by electrochemical methods (OCP measurements, potentiodynamic sweeps, galvanostatic polarization, electrochemical impedance spectroscopy, etc.) on a very small area of about 0.2 mm². The UV-VIS detector downstream of the electrode analyzes in parallel the dissolved amount of an element, and from these dissolution profiles the corrosion current density of the material can be determined directly and compared with electrochemical data. All measurements are fully automated and controlled by in-house programmed *LabView* routines and the SFC was extended as routine tool for the evaluation of corrosion properties in industry laboratories.

Amorphous and nanocrystalline Fe-based materials have been targeted as unique model alloys for fundamental corrosion research. The stainless-type alloy system Fe_{65-x}Cr_xMo₁₄C₁₅B₆ can be reliably produced in the ultimately homogeneous amorphous

state as well as, by applying specific heat treatments, in partially (to a varying extent) or fully crystallized versions. The very short length scale of the formed inhomogeneities renders these materials ideally suited for high-resolution techniques such as Atom Probe Tomography and Scanning Auger Electron Microscopy, which provide an unprecedented detail of the elemental distribution. The associated well-characterized surfaces serve as the starting point for further unique electrochemical corrosion experiments. In this respect the Scanning Flow Cell ICP-MS setup could provide simultaneous current-voltage measurements and time-resolved individual elemental dissolution behavior. By combining a unique set of experimental techniques an entire corrosion process could be thus followed from the atomic bulk structure right into the electrolyte (see p. 123).

Stability of metal alloy surfaces and in particular dealloying reactions is another important corrosion-related topic studied in the department.

Noble metal binary alloys constitute here the main set of addressed samples. Originally such alloys were studied to understand dealloying-related stress-corrosion cracking in brass materials - nowadays the nanoporous noble metal structures that can be obtained by dealloying have direct technical applications from sensors and actuators to catalysis and batteries. Utilizing a well-studied sequence of surface structural transitions on Cu₃Au(111) we could gain a deeper insight in the working mechanisms of the dealloying process [10]. Further control of the surface processes and resulting morphology of the dealloyed layers could be obtained using corrosion accelerators such as halide additives and inhibitors such as plasma-polymer films or applied self-assembled thiol or selenole layers. The obtained knowledge may be very helpful in creating microstructured porosity especially for sensor applications or microreactors. In particular the thiol-modified surfaces opened up completely new views on initial cracking events and thus close back the circle to attempting to understand dealloying and stress-corrosion cracking.

Under practical application of commercial materials in most cases the underlying corrosion mechanisms are very complex, especially during **long-term exposure conditions**. That is the reason why there is up to now no accelerated test available for really reliable prediction of the corrosion performance under real practical conditions, nor a theoretical simulation tool. One key factor that will play a crucial role in determining the long term performance is the heterogeneous nature of most real life corrosion cases. In the framework of a bilateral project with TKSE and a broader set RFCS project, for instance, strong indications were found that the formation of local cathodes and anodes on the micron and submicron scale and their effect on local pH and concentration of dissolved metal cations play a decisive role for determining the protective properties of the growing corrosion product



layer on the alloy, that leads to a certain degree of “passivation” of these otherwise quite reactive materials. For a real fundamental understanding of the underlying mechanisms, however, *in situ* high-resolution methods are necessary. That is why in addition to the work carried out on SECPM, an STM based potentiometric technique, as described in the last report, further methods were developed, such as a combined SECM and SKP system, that allow to perform *in situ* electrochemical investigations and *ex-situ* SKP exactly on the same area. This was at first successfully applied on dedicated aluminium model alloy samples (see [11-13]). Also first steps for the simulation of the surface pH have been carried out [14,15]. Another important project was to investigate the beneficial role of Mg cations on inhibiting oxygen reduction on cathodically polarized iron, in order to understand the reported excellent performance of zinc-magnesium alloy coatings at the cut edge or scratches down to the steel. It could be shown that the significant protective effect found at early stages is not correlated to an improved precipitation layer of corrosion products, but rather to a direct modification of the iron oxide [16].

In the understanding of the **initial stages of corrosion processes under aqueous environments**, the electronic structure of the forming corrosion products is crucial for charge and material transport and the consequent development of the corrosion reaction. A novel analysis scheme for *in situ* spectroscopic ellipsometry has been developed to enable a model-independent extraction of layer thicknesses and absorption spectrum of the forming, nm-thick layers. Results for zinc in carbonate show the presence of two different time scales in the layer growth, the formation of ZnO is decoupled from the formation of an oxidation layer [17]. Further application to copper in different media shows *in situ* the formation of oxides in different oxidation stages, depending on the conditions.

Moreover, the **electrochemical properties of the oxide layers** play a key role in the corrosion behaviour of metals and metal alloys. Within the reporting period it was investigated how different surface treatments of aluminium change the properties, especially the position of the Fermi level [18,19]. For the corrosion performance of zinc alloy coatings at the cut edge, the properties of the iron oxide on the exposed iron or steel was identified to determine the corrosion rate of the zinc alloy. Strong indications were found that zinc cations exchange with reactive Fe²⁺ sites in the oxide, thus significantly inhibiting oxygen reduction. This inhibition is synergetically enhanced by the presence of magnesium cations (see [16]).

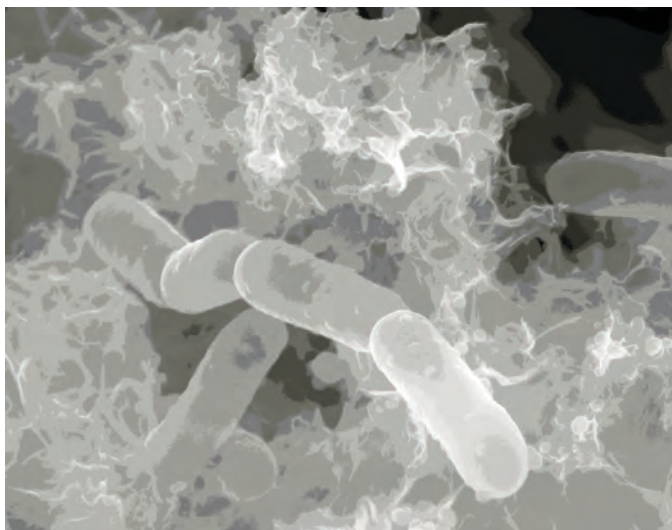


Fig. 3: Sulfate-reducing bacteria (*Desulfopila corrodens* strain IS4) in their extracellular polymeric substance on an iron substrate causing anaerobic microbially influenced corrosion.

Biocorrosion of iron that arises in anoxic environments is predominantly ascribed to anaerobic microbially influenced corrosion (MIC), with marine sulfate-reducing bacteria (SRB, see Fig. 3) being the major contributors [20]. Anaerobic MIC causes serious damages in the oil and gas industry, thus assessing and monitoring of corrosion problems and also elucidating the yet unresolved corrosion mechanism is of great importance. In close cooperation with the Max-Planck-Institute for Marine Microbiology in Bremen we work on quantifying corrosion rates *in-situ* and gaining a more detailed insight into the fundamental electron transfer mechanism at the electrode/bacteria interface. Therefore SRB strains with high corrosion activities in comparison to other well-investigated strains are studied in a multidisciplinary approach utilizing electrochemical techniques, surface analytics and molecular biological methods.

Adhesion, thin films and friction

In **modern corrosion protection systems**, the concept of inhibitor release from capsules incorporated into metallic coatings is one important direction. Mesoporous SiO₂ is a well-suited material, however, its incorporation into metallic layers, e.g. Zn, in the electrogalvanisation process, proved to be challenging. By modification of the particles with silanethiols, the metal/oxide interface energy is modified accordingly to enable an incorporation into the growing metal [21]. Incorporation is only observed above a critical radius [22]. Besides, a thorough characterisation of genuine bifunctional silane monolayers for use as adhesion promoters on oxide-covered Si was conducted [23]. This work attracted considerable attention and was the most downloaded article in Appl. Surf. Sci. in summer 2012.

As chromating is already widely banned and now also **phosphating** is foreseen to be applied to much lesser extent in the near future, the interface between organic or hybride organic-inorganic coatings and the metal surface become more and more important. **Delamination at such interfaces is one of the key expertises of the department.** However, while in the past the focus was mainly on the fundamentals of delamination from plain metals such as zinc and iron, delamination from multiphase zinc alloy coatings, for instance, requires approaches with much higher resolution. For this the Scanning Kelvin Probe Force Microscope (SKP-FM) of the department was modified for dedicated *in-situ* experiments on delamination. First experiments were successfully performed on filiform corrosion and it could be shown that cathodic delamination at the head of the corrosion filaments can play a crucial role in coupling the anodic head with micron size active cathodic sites at the interface [24,25]. Another approach for better understanding is to simulate polymer/metal interfaces by preparing well defined terminations of the oxide layer and studying the effect on the properties of the resulting interface with polymers [26].

In this respect also **molecular forces at electrochemical interfaces** play a critical role in understanding and ultimately preventing adhesive bond failures in materials applications. In collaboration with the University of California at Santa Barbara (Prof. J.N. Israelachvili) we developed two newly designed experiments: the **Electrochemical Surface Forces Apparatus (EC-SFA)** [27] and a **novel electrochemical AFM** [28] **setup**, which uniquely provide *in-situ control of surface potentials and interfacial electrochemical reactions* and a simultaneous measurement of normal interaction forces, friction forces, distances and surface separations as well as contact shapes between dissimilar apposing surfaces. Using the EC-SFA setup we showed that surface morphology and in particular nanoscale roughness significantly altered the effective counterion distribution and measured force profiles at electrified interfaces. Moreover, the EC-SFA allowed for the *in-situ* structural identification and characterization of electrochemically growing (or modified) oxide thin films. In particular, the thickness of anodically growing oxide films was measured *in situ* with Å-accuracy on rough and smooth surfaces. Finally, we performed **potential dependent friction force measurements** [29] at electrode-ceramic contacts that revealed a dramatically increased shear viscosity at electrified interfaces, which is likely due to migration and redistribution of ions at the interface and restructuring of water into solid-like layers. The development of the EC-SFA tribocorrosion and in particular analysis of damage occurring under tribological conditions will further extend our portfolio in the next years. The EC-SFA provides the means to simultaneously correlate

thin film rheological properties, interaction forces (adhesion and friction) and interfacial electrochemical reactions at electrified interfaces.

Functional surface and interfaces

The development of **coatings for corrosion protection** within the department focuses mainly on the application of conducting polymers and particle modified zinc coatings. It was found that in principle three different cases exist for metal coatings based on conducting polymers: enhanced corrosion where the conducting polymer oxidises the metal and the conducting polymer in turn is re-oxidised by oxygen from the air; a passive interface with electronic contact between metal and conducting polymer, which is the targeted situation as it allows a corrosion triggered release of self-healing agents; and a situation where electronic contact between metal and conducting polymer is lost, leading to Fermi level misalignment between these two. The first and the last cases have both to be avoided. A simple SKP based screening method was developed for characterising the different coating systems in regard to these three cases and first models are proposed to explain the underlying mechanisms [30]. This will play an indispensable role for developing reliable coating systems. The storage of active substances inside the zinc (alloy) coating is considered to be of central importance for ensuring self-healing coating systems that will be fully operative even after long term exposures: the more reactive components, such as catalysts initiating polymerisation of monomers released from the organic coating, will be safely stored in the zinc (alloy) coating that is impermeable for water or oxygen. The synergy between agents stored in the zinc coating and an organic or inorganic-organic hybride coating is also the central concept of the MPG-FHG cooperative project on active corrosion protection (ASKORR) carried out together with MPIP, SIC and IAP (see report on ASKORR). One of the main problems for the storage of capsules in zinc, the difficulty to electrodeposit water dispersable capsules into zinc coatings, was successfully overcome [21].

A **molecular level understanding of interaction forces** and dynamics between *asymmetric* opposing surfaces in water plays a key role in the utilization of molecular structures for functional and smart surfaces and coatings. To quantify interaction forces and binding dynamics between opposing surfaces in terms of their chemical and molecular design we developed a novel surface forces apparatus experiment, utilizing molecularly smooth self-assembled monolayers (SAMs). Varying the SAM headgroup functionality allowed us to quantitatively identify which interaction forces dominated between the functionalized surfaces and a surface coated with a precisely controlled number density of short-chain, amine end-



functionalized polyethylene-glycol (PEG) polymers. We could directly quantify and distinguish (a) specific bindings, (b) steric effects of polymer chains and, (c) adhesion of the polymer backbone, all as a function of the solution pH. Combined with novel synthetic approaches this newly developed concept will allow a very accurate molecular quantification of binding interactions between arbitrary chemical functionalities, and polymer backbones with surfaces [31].

Industrial processes

In outdoor applications **conversion coatings** constitute a fundamental cornerstone for corrosion protection. Traditionally, phosphating is employed. Novel steel surfaces containing oxides, which cannot be attacked by pickling, are difficult to phosphate. On the other hand, passivating oxides may be relevant candidates for providing corrosion protection through grain boundaries in the phosphate coating, which would supersede the use of nickel in the baths. Using electrochemical phosphating, fully phosphate-covered surfaces on Al/Si surfaces could be obtained. Currently, their corrosion protection performance is under investigation. A new project was started on nanoceramic conversion coatings together with Henkel AG & Co. KGaA, investigating the behaviour of the future pretreatment systems under electrochemical polarisation.

Moreover, **zinc based metallic coatings** are of tremendous importance for corrosion protection and are object of research since decades. Besides others, salt spray tests have been used extensively for this purpose by applied researchers, providing however only a partial picture of corrosion processes under actual environmental conditions. The novel high-throughput screening approach based on a microelectrochemical flow cell system is able to deal with the issue of the complex interrelation between many experimental parameters, in particular the variable ion composition of salts. For this purpose the setup has been extended for fully automated switching between electrolytes while still enabling a

facile coupling with downstream online analytics. In a strong collaboration with Arcelor Mittal/OCAS this is utilized first of all to increase our understanding of the impact of the electrolyte components on the fundamental corrosion mechanism and kinetics, and shall finally lead to enable tailoring of corrosion protection coatings with respect to the exposure conditions.

Hot dip galvanising is another industrial production step, which is intensely investigated within the department. At the focus in the last two years were co-segregation effects of alloying elements in surface oxide formation [32-34] and effects of oxygen partial pressure not only on the wetting properties of liquid zinc but also on the subsurface structure and its mechanical properties [34-36]. Especially noteworthy is the development of a **novel thermo-balance set-up** that allows measurements even during fast heating and cooling steps (see thermo-balance highlight), such as, e.g., during recrystallization annealing before hot dipping. This set-up was developed within the RFCS project "HEAT" where the aim is to grow an ultra-thin iron oxide layer during soaking that serves as diffusion barrier for alloying elements.

Fundamental problems of **oxidation and hydrogen uptake during industrial production** steps of high strength steel sheet are at the focus of the Christian Doppler Laboratory of Michael Rohwerder [37-41]. Significant advances on developing a novel method for hydrogen detection based on SKP were made (see p. 119) [39]. Further, the thermodynamic simulation tool developed within the CD lab (see p. 137) was applied to different key issues. Hydrogen uptake during high temperature production steps, such as, e.g., recrystallization annealing was investigated in detail. Based on *ex-situ* [42] and *in-situ* (ambient ESCA performed at BESSY) analytical investigations we could show that the hydrogen uptake is correlated to the effective oxygen coverage of the surface and that some alloying elements such as Mn can decrease the water dissociation reaction, which results in lower oxygen coverage and higher hydrogen uptake.

Scientific Groups

Electrocatalysis (Karl J. J. Mayrhofer)

The research interests of the electrocatalysis group (www.mpie.de/ecat) are related to electrochemical reactions at the solid-liquid interface, both for corrosion processes and electrochemical energy conversion. The main focus of the group is placed on the concerted investigation of the activity, stability and selectivity of electrode materials for such heterogeneous electron-transfer reactions. Thereby the behaviour of well-defined and real material surfaces are investigated and compared

in order to achieve a fundamental understanding of the decisive processes and structural effects. This is achieved by a unique combination of electrochemistry with complementary techniques for surface characterization and reaction product determination.

Technically, the group is developing new electrochemical methods to investigate model and applied electrode materials. High-throughput combinatorial screening tools combined with sophisticated automation and synchronization of the experimental setup (see Fig. 2), as well as advanced methods

for data evaluation and processing play thereby a major role [43]. This enables investigation of a large number of samples more systematically and reliably in shorter time. In addition, coupling electrochemistry with online reaction product determination by Inductively Coupled Plasma Mass Spectrometry [4,5] and Differential Electrochemical Mass Spectrometry (DEMS, see p. 18) increases the information depth significantly.

Besides these technical advancements, we are interested in various topics in electrocatalysis that we address with our advanced techniques. Together with the group of A. Auer we are investigating the H_2O_2 reactions as an important intermediate in the oxygen reduction reaction (see p. 129) [1,2]. Other important aspects in our research are the influence of the surface pH [14,15] and the effect of the electric double layer on the adsorption of reaction intermediates and the reaction kinetics itself. The latter becomes especially important when considering the effects that determine the activity of supported nanoparticle catalysts or de-alloyed, porous catalysts, since they behave quite different from extended surfaces [44,45]. CO_2 utilization by electrochemical means for the production of so-called solar fuels is a further hot topic in our group related to energy conversion and storage, and will be investigated in our new laboratory (p. 18) [46].

The conditions during these reactions at the solid-liquid interface are often quite harsh and lead to corrosion of the electrode material. Therefore, particular research focus in our group is placed on fundamental and applied aspects of stability. We investigate online, and in parallel to the activity, the dissolution of elements under different experimental conditions to derive the determining steps in the mechanism, and quantify the individual element contribution to the overall dissolution. This is not only of high value for noble electrocatalyst materials based on Pt or Rh, but is also of great importance for complex materials like steels (see p. 123), ZnO for photovoltaic applications [47,48] or protective coatings based on Zn/Mg/Al. Moreover, utilizing our Identical Location – Transmission Electron Microscopy approach we study the degradation of high surface area catalysts as well as de-alloying phenomena and porosity formation on the nanoscale (see p. 131) [49,50]. In collaboration with the Max-Planck-Institut für Marine Mikrobiologie in Bremen we investigate the anaerobic corrosion of iron and steel by sulfate reducing bacteria (see Fig. 2).

Atomistic Modelling (Alexander A. Auer)

Atomistic modelling of electrochemical processes, interfacial properties and novel materials are central aspects in the work of the atomistic modelling group. Besides on-going method development in the field of post-HF *ab initio* method [51] computational studies in close collaboration with experimentalists yield insight into complex phenomena, as simulations can be used to complement experimental results from surface science and spectroscopy.

One example for this is the work on the oxygen reduction reaction on various substrates like Pt nanoparticles (see highlight ORR). The segregation behaviour of Platinum Cobalt core shell particles had been investigated previously by Mayrhofer et al., who found that Co-core Pt-shell particles can be obtained by CO annealing and that upon electrochemical treatment in the ORR the lesser noble metal is leached out. A theoretical investigation was carried out on a Pt-NP model system in which favourable and less favourable Co-substitution sites were identified. Furthermore, the influence of Oxygen and CO on the segregation energies were investigated [52]. The results do not only confirm experimental findings but also yield insight into a stepwise segregation mechanism in which the fact that NPs are fairly ductile systems plays an important role.

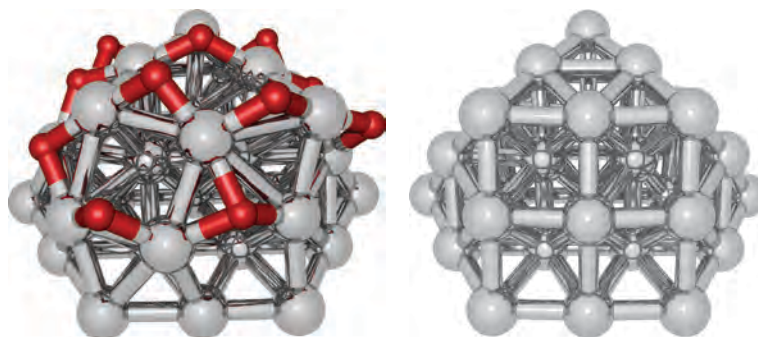


Fig.4: Ductile system: Pt37 model system exhibits the properties of small nanoparticles, upon oxygen adsorption significant distortion of the system occurs.

DFT calculations using nanoparticle-models prove to be very versatile as they can be used to investigate intermediates of the ORR as well as material properties of real catalysts (see Fig. 4). In further investigations fundamental questions have been studied concerning schemes to model the electrochemical potential for nanoparticle systems [53]. Theoretical approaches to describe electrochemical processes including the influence of the solvent and electrode potential have been further developed and applied to the ORR mechanism at highly active metal catalysts as well as semiconducting interfaces.

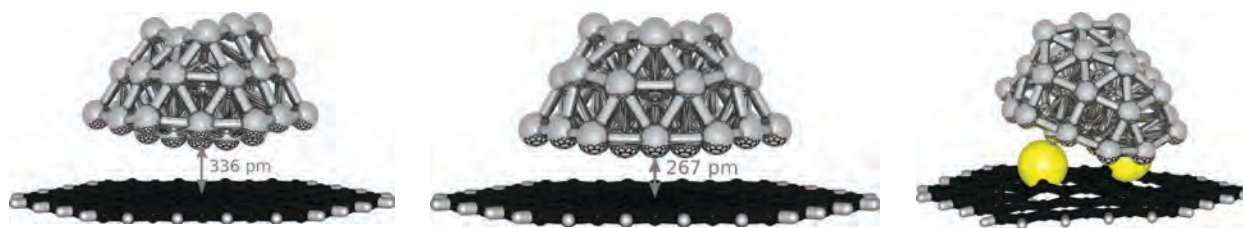


Fig. 5. Interaction of the Pt₃₇ cluster with a graphitic carbon support model – classical DFT result (left), DFT-D with inclusion of dispersion correction (center) and with sulphur as linking unit (right). As the linker also acts as a spacer, reducing the dispersion interaction, the adhesion is actually decreased in this case.

Furthermore, problems in the application of NPs, which often are used in conjunction with carbon support, have been investigated (see Fig. 5). A computational study of the metal-carbon interaction shows that it is not only vital to apply state-of-the-art dispersion interaction corrected DFT approaches but also that the main bonding mechanism is based on weak interactions with the support. For experimentalists this work yields insight into the basic adhesion mechanisms and how functionalization of the support can be carried out to improve the adhesion of the particles [54].

Extending previous work on the ZnO(0001)/water interface a Ph.D. Thesis has been launched to characterize the non-polar ZnO(10-10) and (1120) surfaces as well as the polar ZnO(000-1) surface interacting with water in order to gain a complete picture of the surface properties of this important material in corrosion protection, and catalysis under in-operando conditions as basis for future adhesion and corrosion studies. Building on the acquired expertise on ZnO surfaces, the ORR mechanism on ZnO(10-10) has been analyzed using a cluster model for the interface. Comparison to the mechanism in homogeneous solution allows to quantify the electrocatalytic properties of this surface.

In the framework of the Forschergruppe 1497 “Zwillingspolymerisation von Organisch-Anorganischen Hybridmonomeren zu Nanokompositen” a series of investigations has been carried out in order to understand the basic mechanism of the twin polymerisation [55]. This novel technique allows to synthesize inorganic/organic hybrid materials with domain sizes in the range of a few nanometers. This reaction has been intensively investigated during the last years from which SiO₂/Phenol resin nanocomposites, for example, can be obtained in a single step synthesis from one type of monomer. Novel approaches using Ga or Ge oxides as inorganic component might open the route to materials with high potential for application in various fields [56].

The very fruitful collaboration with the group of Prof. K. Banert from the organic synthesis group at

the TU Chemnitz has lead to a series of successful projects focusing on the synthesis of novel compounds that have witnessed quite some interest in the literature. These have been published with title pages in *Chemistry - A European Journal* in 2011 and in *Angewandte Chemie* in early 2012 [57,58] and demonstrate the versatility of applications for accurate electronic structure calculation (see Fig. 6).

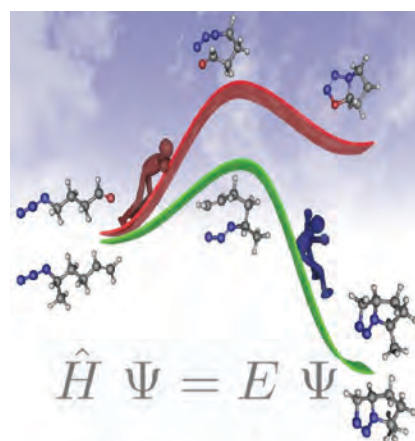


Fig. 6: Accurate *ab initio* calculations reveal possible reaction paths and can help to guide experiments as well as correct synthesis for which products have been misinterpreted.

In collaboration with Bayer Leverkusen and ICAMS multiscale modelling techniques have been developed to simulate the network formation and mesoscale structure formation processes during the curing of polyuretanes. A detailed coarse-grained (mesoscale) simulation including accurate conformational and intermolecular interactions as well as reactivity was developed based on DFT and atomistic force-field calculations and calibrated against available experimental data. Future work will also include the reactivity at, e.g., ZnO surfaces and interphase formation to better understand adhesion and to develop an atomistic interface model for studies of mechanical properties, reactivity with environmental agents, deadhesion, and corrosion.

Interface Spectroscopy (Andreas Erbe)

The Interface Spectroscopy Group continues to work in two different directions, (1) the design of interfaces for spectroscopic investigations with their application to the study of electrochemical reaction mechanisms and (2) chemical modification of material's interfaces to tailor surface properties and to investigate failure mechanisms.

The theoretical optical part has progressed the understanding of infrared spectroscopic experiments from rough interfaces [59,60]. Using finite element solutions of the Maxwell equations, details emerge which regions of an interface with complex morphology are actually accessible to light [60]. Transparency of thin continuous metal films was enhanced through the application of anti-reflection coatings on the metal [61]. A further improvement of the scope of infrared spectroscopy at interfaces can be achieved through the use of intense tunable laser light sources. A first step in our lab was the establishment of a reflection setup involving a pulsed, tunable quantum cascade laser [62].

In the ultraviolet and visible spectral range, spectroscopic ellipsometry was used to study the evolution of oxide on zinc *in situ* (see p. 133) [17,63]. Both in oxygen-containing and oxygen-free atmospheres

[63], as well as in electrolyte [17], the evolution of the layer thickness is decoupled from the evolution of the electronic structure of the layer. The electronic structure is probed through the absorption spectrum at photon energies between 1 and 4 eV.

A collaboration was established with the group of Patrick Koelsch, formerly at Karlsruhe Institute of Technology, now at University of Washington, Seattle, who is an expert in modern vibrational sum-frequency-generation (SFG) spectroscopy. Complemented by ellipsometric analysis at MPIE, femtosecond-broadband SFG spectroscopy was applied to electrochemically highly stable araliphatic self-assembled monolayers (SAMs), which was studied extensively in the group "Molecular Structure and Surface Modification" [64,65]. The SFG results show on the one hand the surprising maintenance of ordered structures after electrochemical desorption of the SAMs [64]. The detection of a mixing of the static electric field with the SFG signals may enable a direct access to the interfacial electric field in the future [65]. Details of these results are presented as a highlight in this report. A collaboration with the Institute of Physics, Academia Sinica, Taiwan, resulted in the fabrication of a ~5 nm wide gap between tip metal electrodes, which have been used to trap protein molecules for Raman spectroscopic studies [66]. In the future, such devices will enable electrochemical experiments with ultralow sample amounts.

On the chemical surface modification side, in collaboration with industrial partners, work on conversion coatings is performed. An electrochemical, fluoride free process was developed to enable phosphating of oxide-covered Al/Si metallic coatings (Fig. 7). In a new project, properties of modern conversion coatings under the application of electric fields are investigated. Electrocatalytic properties of gold towards methanol oxidation were studied, and a method based on lead deposition used to remove organic material from the electrode surface [67]. While adhesion promoters on silane-basis are long known in industry, their adsorption often results in ill-defined multilayer structures. Systematic investigations of the adsorption resulted in the establishment of a protocol to form well-defined monolayers, which were thoroughly characterised [23]. Such structures are currently being exploited for molecularly defined anchoring of polymer coatings on oxidic surfaces. In cooperation with Max Plank India Fellow Pritam Deb of Tezpur University, a central university in India, chemical surface modification with organic materials of different iron oxide particles was and still is investigated [68].

In a new project within the framework of the Marie Curie Initial Training Network (ITN) "Somatai", diffusion in novel water-based coatings will be investigated. Somatai will be a new opportunity to

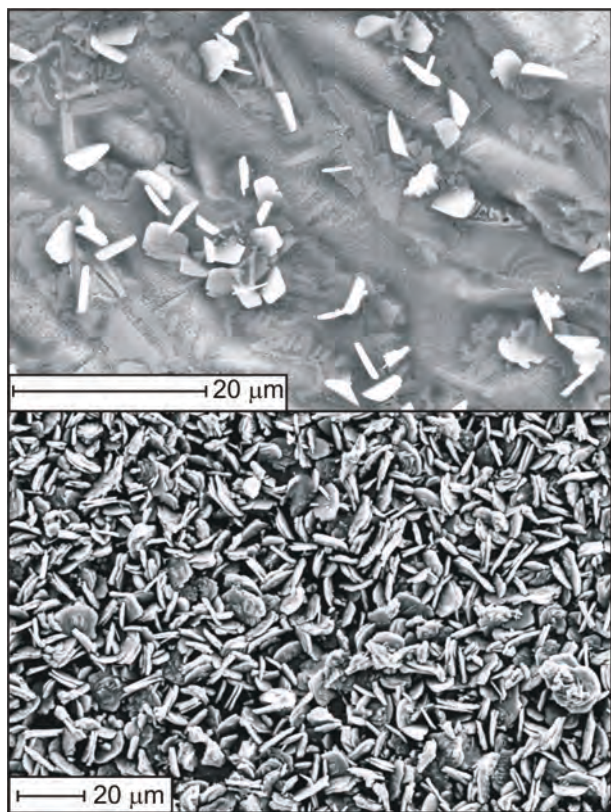


Fig. 7: Two different stages of the phosphating process of AS steel.



link our activities to partners from the soft matter community. The understanding of polymer-based coatings will certainly benefit from this project. As the Somatai website will be hosted at MPIE, we will be involved in the ITN at a central position.

In addition, we provide support to the institute in application of optical characterisation techniques, and with know-how on the properties of light. An important example is the optical characterisation of biological photonic structures in collaboration with the Department of Microstructure Physics and Alloy Design (see p. 139).

Christian Doppler Laboratory for Diffusion and Segregation during Production of High Strength Steel Sheet (Michael Rohwerder)

The main focus of this lab is on fundamental diffusion and segregation problems encountered during the different production steps of high strength steel sheet. Cooperation partners are voestalpine and TU Wien.

The technical motivation behind this is that the development of high strength steels with their characteristic alloying element composition leads to new challenges for the production and processing of steel sheets in order to meet the product requirements. The focus here is on selective grain boundary oxidation during hot rolling and its consequences for pickling, and on hydrogen detection and its uptake kinetics in different process steps. The related questions are of significant scientific interest and the related research of considerable experimental challenge. In sum these problems are addressed within the lab in three modules:

SE (Selective Enrichment) Module:

Within this module the activities focused mainly on two approaches: fundamental investigation of grain boundary oxidation based on dedicated model alloys (see Fig 8) and developing a new simulation tool for describing grain-boundary oxidation on a theoretical level [39-41]. One important result found within the reporting period was that it is mainly the interaction between some of the key alloying elements in high strength steels that is responsible for significantly enhanced internal oxidation. This is at the focus of current research and will be investigated experimentally and theoretically.

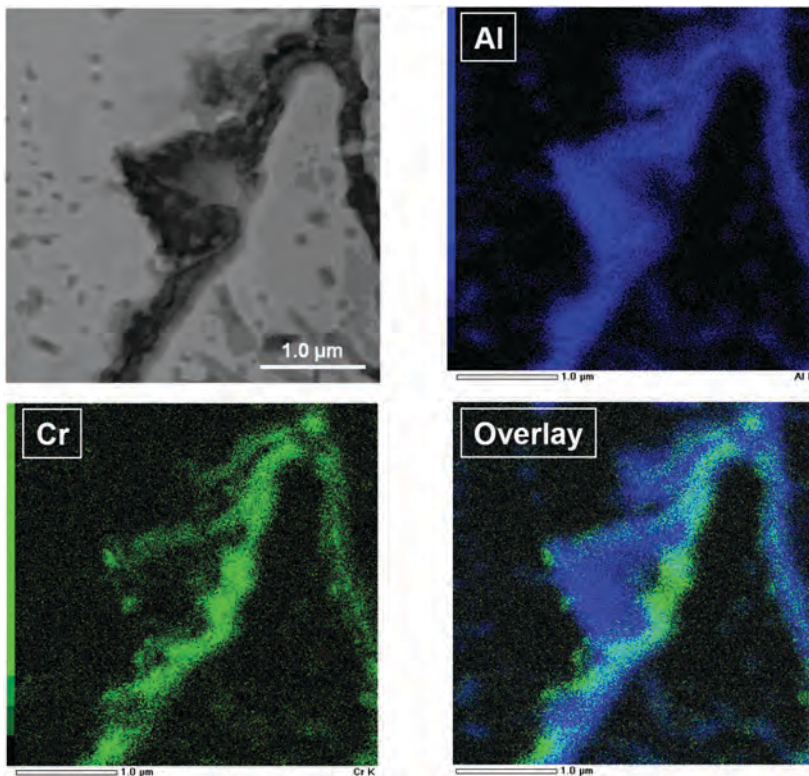


Fig. 8: Layered structure of a grain boundary oxide: EDX elemental maps of a FIB-prepared TEM (cross-sectional) lamella of ternary Fe-3Al-0.8Cr model alloy annealed at 700 °C, in $N_2/2.5\%H_2/9000ppmH_2O$, for 2 hours.

P (Pickling) Module:

This module deals with pickling after hot rolling and is carried out mainly at the TU Wien (Prof. Danninger).

H-Module:

The hydrogen uptake of the material is a significant problem especially for high strength steels, as small amounts of hydrogen in the range of ppm can cause retarded brittle fracture. Uptake during several wet processing steps as well as corrosion and recrystallization annealing is investigated. For the latter an important question is information about the distribution of oxides at the different stages of the annealing [42], which is now also investigated by ambient ESCA. Here a main focus in the reporting period was the successful development of a novel method for spatially resolved highly sensitive hydrogen detection (see p. 119 and [37,38]).

Molecular Structures and Surface Design (Michael Rohwerder)

The main scope of this group is to address fundamental questions of surface and coating technology by isolating the crucial problems behind them and designing model experiments and model samples for their systematic investigation. A technique of central importance for many research projects within the group is the Scanning Kelvin Probe technique. Based

on the world leading expertise in this technique also novel application fields are explored.

The correlated main activities on these research interests can be summarized as follows:

1. *Elementary steps of electrochemically driven de-adhesion of organic coatings*

Two main approaches are used in the group for studying the fundamental steps of delamination. One is to apply Scanning Kelvin Probe Force Microscopy (SKPFM) for studying microscopic and submicroscopic processes during delamination, the other is to investigate the effect of modifications of the surface oxides and/or the functionality of the organic coating on the delamination behaviour. The latter is mainly done by investigating the effect of well characterised self-assembled monolayers. In cooperation with Prof. Wöll (KIT) and Prof. Terfort (Univ. of Frankfurt) our investigations on oxygen reduction at self-assembled thiol monolayer films are extended on a broader base of various aromatic thiol molecules. In order to establish the targeted structure-reaction correlation on the molecular and nanoscopic scale a thorough characterisation of the monolayers is carried out [69,70].

The investigations on monolayer stability provided also extremely interesting results on hydrogen evolution at organic layers and on metallization of self-assembled films. The hydrogen evolution reaction seems to be enhanced at the first stages of cathodic monolayer desorption, which is due to the prevailing molecular order of the film directly after desorption (see p. 135).

Side results of this work were the development of a novel approach for optimizing the complexation of metal cations on self-assembled monolayers and their electro-less reduction by hydrogen (see highlight report), which provides metal monolayers of superior properties [71,72]. The effect of different pre-treatments on the interface with different coatings was studied in detail for aluminium [26]. SKPFM was very successfully applied on filiform corrosion and it could be shown by performing the experiment under repetitive gas change conditions (between air and nitrogen) that cathodic delamination at the head of the corrosion filaments can play a crucial role in coupling the anodic head with micron size active cathodic sites at the interface [24,25].

2. *Semiconducting properties of surface oxide films*

The Kelvin probe technique directly provides information about the work function of the surface oxide, which can be interpreted also as electrode potential. In how far predictions about the possible localised corrosion behaviour in a corrosive environment may

be made from potential maps obtained by SKP in air is the topic of a joined project with Prof. Schuhmann (RUB), where SKP and SECM (Scanning Electrochemical Microscopy) could already be successfully combined [12,13]. This enables application of the SECM exactly on the same features as mapped by SKP. This technique was first applied to aluminium alloys [11]. Further it was investigated how different pretreatments, such as alkaline and acidic cleaning, change the semiconducting properties of the alumina layer. A strong correlation between OH fraction and Fermi level position in the oxide was found [18,19].

Another important topic are novel Zinc-Aluminium-Magnesium alloys (ZAMs) where in earlier works the native oxide layer was shown to play a crucial role in the delamination behaviour. For blank corrosion the properties of the corrosion product layers that grow during exposure are widely assumed to determine the corrosion performance. In many corrosion tests especially the presence of magnesium in the alloys is found to provide significantly enhanced corrosion behaviour. However, the exact reasons are still not known. In the reporting period strong indications were found that the microstructure induced by alloying with magnesium may play a crucial role here, as it determines the lateral distribution of cathodic and anodic sites and hence the local pH, which in turn will have an effect on the growth of the corrosion product layer. Hence, prediction of surface pH is very important and first steps were undertaken [14]. The most important finding of the latest activities, however, was that at the cut edge or at defects down to the steel, the beneficial effect of magnesium at least at the initial stages of exposure is mainly due to enhancing the effect of the zinc cations, which were found to replace reactive Fe^{2+} sites in the iron oxide layer and thus significantly decrease the oxygen reduction rate [16].

3. *Wetting and interfacial reactions at metal/metal melt interfaces and selective oxidation:*

Our research on the reactive wetting behaviour of liquid zinc on a variety of steels and model alloys has provided new insight into the wetting kinetics and how it depends on oxide morphology. At the focus in the last two years were co-segregation effects of alloying elements in surface oxide formation [32-34] and effects of oxygen partial pressure not only on the wetting properties of liquid zinc but also on the subsurface structure and its mechanical properties [34-36]. A big success was the development of a novel thermo-balance set-up, where the reaction gas atmosphere is adjusted without carrier gas and thus works under sub-atmospheric pressures but with the same dew points and hydrogen partial pressures as applied in standard experiments. That allows measurements even during fast heating and cooling steps, such as, e.g., during recrystallization annealing



before hot dipping, without buoyancy forces and with nearly no disturbances at all (see p. 137). This set-up was developed within the RFCS project “HEAT” where the aim is to grow an ultra-thin iron oxide layer during soaking that serves as diffusion barrier for alloying elements.

4. Intelligent self-healing concepts for corrosion protection

The main activities on self-healing are carried out in two projects: a DFG SPP (“Self-Healing Materials”) and a MPG-FHG cooperative project on active corrosion protection (ASKORR). While the first is mainly focused on conducting polymers, the latter is set to synergistically combine capsule loaded zinc coatings with capsule loaded organic coatings for superior intelligent self-healing. Currently the main activity in the first project is on getting conducting polymers work on zinc, where conducting polymers were shown to be usually de-activated [30]. In ASKORR, after solving key issues of particle co-deposition during electro-galvanising [21], the main focus is now on realizing optimized self-healing by a synergetic inter-play of zinc and organic coating (see p. 127).

5. SKP as a tool for general application for processes at buried interfaces

Besides using the SKP technique for *in-situ* investigations in synchrotron set-ups [73], also spatially resolved high-sensitivity hydrogen detection by Kelvin probe is investigated (see p. 63 (CDL lab) and p. 119).

Interface Structures and High Temperature Reactions (Frank U. Renner)

The research activities within the „Interface Structures and High-Temperature Reactions“ group focus on utilizing high-resolution structural techniques and aim at gaining mechanistic insight in processes, possibly on the atomic scale. Starting from a surface science approach the group activities aim to bridge the complexity gap and pressure gap towards more realistic conditions of processes. This goal is achieved by studying still simplistic surfaces but in realistic environments such as electrolytes or corrosive gas atmospheres. In this line ideally ordered, single-element or (binary) alloy single-crystal surfaces but also systems such as complex, ideally disordered, *i.e.* homogeneously amorphous alloys are studied. Especially beneficial are in this context *in-situ* X-ray diffraction techniques using Synchrotron radiation, but also techniques such as Scanning Auger Electron Microscopy (SAEM) or Atom Probe Tomography. In particular the structural aspects accessed by *in-situ* X-ray diffraction are a valuable complementary addi-

tion to the department’s activities on electrochemical processes. Thus, although working on a broad scope of different subjects from oxide scale formation to Li-ion battery interfaces, the group’s main activities can be summarized as:

1. Using simplified (solid) model substrate systems such as single crystals, thin films, or amorphous/nanocrystalline materials.
2. Employing high-resolution structural techniques such as in-house lab-based Auger Microscopy as well as Synchrotron-based large scale facilities - and possibly *in-situ* studies.
3. The main interest is in the behavior of systems in real atmospheres. In the focus are electrochemical interfaces and solid-gas reactions at elevated temperature.

Dealloying is a specific corrosion process and of large fundamental relevance in other electrochemical processes such as catalysis, too. In particular the binary alloy surface $\text{Cu}_3\text{Au}(111)$ with its very particular sequence of initial structural states [10,74,75] has been used within the group’s research program as a reference system to address the influence of corrosion accelerators [28,76,77] and of inhibition mechanisms [10,28]. Single crystal surfaces modified by self-assembled thiol monolayer films revealed a distinctive cracking failure mechanism with clear crystallographic crack openings, which opened a possibility to actually address the initial stages of crack formation in collaboration with other departments (see, *e.g.*, p. 125). As dealloying of noble metal alloys was also studied early-on in the context of stress corrosion cracking these results bear a large promise for furthering understanding in an ultimately technological context.

With corrosion of amorphous and nanocrystalline steels a further promising research topic could be established. Selective dissolution phenomena in the context of passivity and wet corrosion could be in great detail related to the respective nanostructured materials in collaborations with the Electrocatalysis group (Dr. K.J.J. Mayrhofer) and the Atom Probe Tomography group (Dr. P.-P. Choi, Department of Microstructure Physics and Metal Forming). This approach of using a unique set of complementary methods bears a great potential to actually gain deeper well-characterized insight into the microstructure-performance relation of corrosion reactions and passivity.

Next to further electrochemical reactions such as electrodeposition from ionic liquids (in collaboration with Dr. M. Rohwerder), phosphating (in collaboration with Dr. A. Erbe), or battery processes (see p. 29) also elevated and high-temperature gas corrosion is studied in part with industrial partners in various

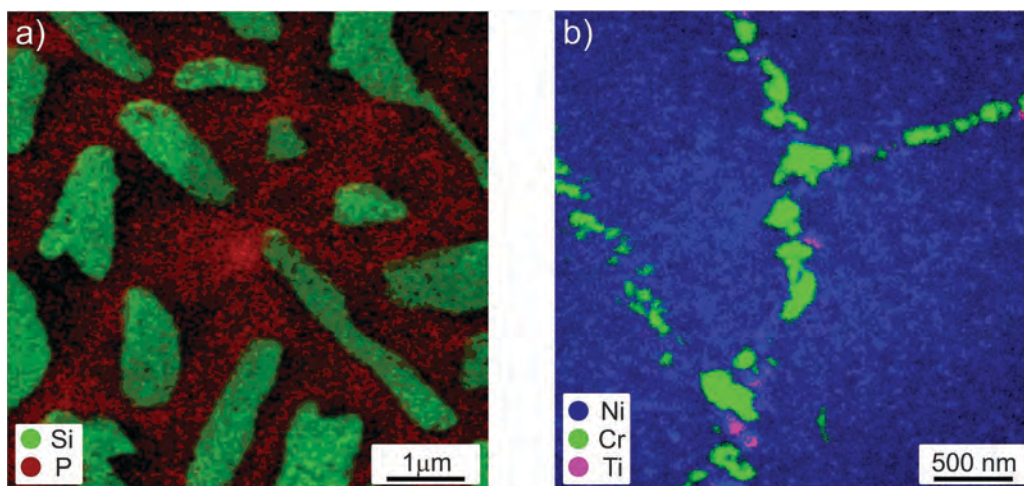


Fig. 9. Scanning Auger Electron Microscopy maps of a) phosphate coverage on an AS-steel surface and b) grain boundary in a Ni-based superalloy.

atmospheres, *i.e.* oxidation, steam corrosion, or sulphidation. These works will be continued using more high-resolution methods and *in-situ* diffraction to study the initial stages of similar processes. Fig. 9 includes two SAEM images showing the selective phosphate reaction on AS steel and a grain boundary prior to sulphidation.

Interaction Forces and Functional Materials (Markus Valtiner)

The research interest and philosophy of the newly established group (www.mpie.de/ifor) is focused on the broad areas of adhesion, friction and interfacial forces, as well as their concerted utilization for making novel smart and hierarchically structured materials, interfaces and thin films for application in structural and functional materials. Our scientific aim is to gain insight into the fundamental interactions of complex interfacial processes, and to translate fundamental science into knowledge-based design of better and novel structural and functional materials for technological applications. We are in particular interested in:

1. Fundamental work on interfacial forces, interfacial structures and tribology under (electrochemically active) variable environmental conditions.
2. The effect of (electro-)chemical reactions on interfacial interactions with a particular focus on structural effects in confined spaces and complex environments (high salt concentrations and non-aqueous electrolytes).
3. Electrochemistry in confined spaces.
4. Measurement, understanding and ultimately prediction of properties of surfaces, interfaces and thin films over large length and time scales.
5. Design and utilization of model experiments and

tunable thin films and interfaces using unique bio-mimetic and molecular design concepts.

6. Development and establishment of new experimental techniques for surface and interface analysis.
7. Preparation and characterization of advanced functional materials with smart properties.

The technological focus of the group is the *design of novel experiments and experimental setups* dedicated to understanding interfacial dynamics such as specific and non-specific binding and unbinding events at the single molecular and macroscopic level. The newly developed electrochemical Surface Forces Apparatus provides the means to experimentally realize confined environments on the sub-nanometer scale. This capability will be extended to study electrochemical reactivity and kinetics in confined spaces. On p. 16, the scientific philosophy of the group and the newly designed EC-SFA are detailed.

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Research Projects in Progress

Electrocatalysis (K.J.J. Mayrhofer)

Baldizzone: Degradation of carbon-supported Pt bimetallic nanoparticles

Beese, Widdel: Anaerobic microbially influenced corrosion of iron

Cherevko, Zeradjanin, Fink: High-throughput material screening for electrochemical CO₂ reduction

Cherevko: Mechanism of electrochemical gold dissolution in acidic media

Cherevko, Topalov, Ankah, Renner: Metal dissolution during electrochemical dealloying: the case of Cu₃Au(111) model system

Hamou, Biedermann, Arenz: EDL influence on reaction kinetics on nanoparticle catalysts

Jeyabharathi, Hodnik: Particle-size dependent dealloying

Katsounaros: Oxygen reduction reaction on noble metal catalysts

Katsounaros, Schneider, Auer: Understanding the mechanism of the oxygen reduction reaction

Laska: Effect of variable electrolyte composition on zinc corrosion investigated by a SFC system with dynamic electrolyte change

Meier: Study of particle size effect on fuel cell catalyst stability under simulated start up/ shut down conditions

Meier, Baldizzone: Influence of thermal pre-treatment of fuel cell catalysts on durability

Meier, Auinger, Katsounaros: Effect of surface pH on the oxygen reduction reaction (ORR) in neutral electrolytes

Meier, Galeano, Schüth: Influence of intrinsic N-doping on activity and stability of hollow graphitic sphere based platinum nanoparticles

Rossrucker: High throughput screening of zinc and zinc-magnesium material libraries with a SFC and downstream analytics

Schuppert: Screening of high-surface-area catalysts for application in polymer electrolyte membrane fuel cells with the SFC setup

Schuppert, Topalov: Activity and stability of PtCu-alloys by screening of thin-film material libraries

Topalov: Stability investigation of Pt and Pt-based alloys utilizing a high-throughput SFC coupled with ICP-MS

Zeradjanin, Cherevko: CO₂ reduction product analysis by SFC coupled with DEMS



Atomistic Modelling (A.A. Auer)

Auer, Schneider, Benedikt: Computational study of precious metal nanoparticle – carbon support interactions

Auer, Schneider, Benedikt: Computational study of the oxygen reduction reaction on Pt and Pt alloy nanoparticles

Auer, Schneider, Benedikt: Model development for describing electrochemical reactions on nanoparticles using quantum chemical methods

Auer, Schneider, Benedikt: Modelling the influence of solvent in electronic structure calculations of electrochemical reactions

Berezkin, Biedermann (in cooperation with ICAMS and Bayer Leverkusen): Multi-scale simulation of polyurethane curing and interphase formation on ZnO substrates

Biedermann: ORR at the ZnO/water interface

Biedermann, Bashir, Rohwerder: DFT simulations of vibrational spectra of SAM molecules

Biedermann, Nayak, Erbe: Intermediates of the ORR on germanium

Chakraborty, Auer, Biedermann, Nayak, Erbe (in cooperation with Rochus Schmidt, RUB): Ge/electrolyte interface structure in function of the electrode potential

Hamou, Biedermann, Mayrhofer: The effect of roughness and porosity on the electric double layer and ORR catalysis

Kenmoe, Biedermann: DFT study of the ZnO/water interface

Salgin, Hamou, Rohwerder: Application of the scanning Kelvin probe for monitoring ionic surface migration

Interface Spectroscopy Group (A. Erbe)

Altin, Ritter, Rohwerder, Erbe: Cyclodextrines as controlled release systems in corrosion protection

Deb, Ebbinghaus, Schneider, Kostka, Erbe: Characterization and surface modification of iron oxide nanoparticles

Ebbinghaus, Lesser-Rojas, Chou, Erbe: Raman spectroscopy at nanoelectrodes

Iqbal, Muhler, Erbe: Preparation of molecularly-defined polymer/metal interfaces and their delamination behaviour

Iqbal, Erbe: Nanostructuring through corrosion

Iqbal, Bashir, Rohwerder, Erbe: Photoswitchable self-assembled monolayers

Moirangthem, Schwenzfeier, Erbe: Surface water and water surfaces studied by infrared ellipsometry

Nayak, Biedermann, Stratmann, Erbe: Detection of intermediates in the oxygen reduction reaction on semiconductor electrodes

Nayak, Sriram, Chou, Erbe: Behaviour of water in confined environments

Pengel, Stratmann, Erbe: Time-resolved infrared spectroelectrochemistry

Sarfraz, Posner, Erbe: Effect of the cathodic electrodeposition coating on nanoceramic conversion coatings

Schneider, Renner, Erbe: Initial stages of crystallization of phosphates on the surfaces of zinc and modern steels

Seemayer, Schneider, Renner, Todorova, Erbe: Corrosion of iron in H₂S-containing sour acid media

Christian Doppler Laboratory for Diffusion and Segregation during Production of High Strength Steel Sheet (M. Rohwerder)

Auinger, Rohwerder: Simulation of selective oxidation and grain boundary oxidation

Borodin, Rohwerder: Investigation of hydrogen uptake kinetics during recrystallisation annealing

Evers, Borodin, Rohwerder: Spatially resolved and ultra-sensitive hydrogen detection in steels and investigation of hydrogen uptake

Auinger, Swaminathan, Borodin, Rohwerder: Fundamental investigation of grain boundary oxidation

Molecular Structures and Surface Design (M. Rohwerder)

Altin, Ritter, Rohwerder, Erbe: Cyclodextrines as controlled release systems in corrosion protection

Ankah, Renner, Rohwerder: Fundamental investigations of de-alloying

Bashir, Krieg, Rohwerder: Characterization of zinc alloys for automotive application

Bashir, Rohwerder: STM, SECPM and SKP for surface characterisation

Iqbal, Bashir, Rohwerder, Erbe: Photoswitchable self-assembled monolayers

Krieg, Borissov, Rohwerder: Investigation of cathodic self-healing at cut-edge, blank corrosion of ZAMs

Liu, Swaminathan, Rohwerder: Fundamental investigation of hot dip galvanizing

Merzlikin, Rohwerder: Characterisation of hydrogen in steels



Muglali, Erbe, Rohwerder: Oxygen reduction, hydrogen evolution and metal deposition at self-assembled monolayer/gold interfaces

NN, Rohwerder: Novel corrosion protection coatings for hot forming

NN, Rohwerder: Guidelines for use of welded stainless steel in corrosive environments

Padhy, Erbe, Rohwerder: Electronic structure of native oxides in dependence on the atmosphere

Salgin, Rohwerder: Mobility along interfaces and on surfaces and effect of modification

Senöz, Bashir, Rohwerder: SKPFM for the investigation of localised corrosion

Tran, Vimalanandan, Rohwerder: Intelligent corrosion protection by nanocapsules incorporated to the zinc coating: understanding co-deposition and synergy with organic coating

A. Vogel, Merzlikin, Rohwerder: Nano-particular iron oxide films for improved wettability

Vogel, Schönberger, Rohwerder: QCM for high temperature application

Vogel, Merzlikin, Rohwerder: High emissivity annealing technique for improved hot dip galvanising

Vimalanandan, Rohwerder: Intelligent corrosion protection coatings by conducting polymers

Interface Structures and High Temperature Reactions (F.U. Renner)

Ankah, Ma, Raabe, Cherevko, Mayrhofer, Rohwerder, Renner: Dealloying of Cu–Au alloys.

Ankah, Renner: Dealloying of Cu–Pd alloys.

Bach, Seemayer, Renner: Advanced characterization of Li-ion battery electrodes

Bashir, Ankah, Klemm, Valtiner, Renner (in collaboration with M. Valtiner): In-situ AFM studies of selective inhibition by thiol u-contact printing

Duarte, Kostka, Choi, Raabe, Renner: Bulk segregation in heat treated amorphous steels

Duarte, Renner: In-situ high-energy X-ray diffraction of crystallization of amorphous steel

Izzuddin, Renner: Sulphidation of Ni–Al alloys

Klemm, Duarte, Mayrhofer, Renner: Element-resolved corrosion studies

Lange, Rohwerder, Renner: Grain boundary sulphidation of Ni-based alloys

Lymperakis, Neugebauer, Renner (in collaboration with CM-Department): Atomistic simulations of a Au/Cu–Au heterophase interface

Madinehei, Duarte, Klemm, Crespo, Renner (in collaboration with BarcelonaTech, Spain): Production and corrosion of low-Cr amorphous steel.

Schneider, Lange, Erbe, Renner: (in collaboration with A. Erbe): Surface analysis of initial stages of phosphating reactions

Seemayer, Bach, Renner: Model systems for Li-ion batteries

Vogel, Palm, Renner: High-temperature corrosion of iron aluminides in steam

Interaction forces and functional materials (M. Valtiner)

Valtiner: Unravelling of structure/property relationships at electrified interfaces

Baimpos, NN, Valtiner: Electric double layer structures in highly concentrated electrolytes

Baimpos, Valtiner: Development of novel molecular force sensors

Raman, Stock, Valtiner: Design, synthesis and testing of novel adhesion promoting bio-molecules for superior wet-adhesion

Raman, Stock, Valtiner: Single molecule physics at electrified interfaces

Department of Microstructure Physics and Alloy Design

D. Raabe

Scientific Concept

We conduct basic research on the relationship between synthesis, structure and properties of materials, Fig. 1. The focus lies on nanostructured engineering alloys based on iron [1], magnesium [2,3], titanium [4], nickel [5,6], and intermetallics [7] as well as on biological [8] and metal-based composites [9]. Recently, also interfaces in semiconductors are studied [10-13]. These materials and their mechanical properties are characterized by complex phase transformations [14] and defect substructures [15]. To study these phenomena and their interplay we develop advanced characterization methods from the single atom level [1,14] up to the macroscopic scale and apply them together with scale-matching multiscale models, Fig. 2 [16]. Examples of experimental tools are local electrode atom probe tomography [1, 14, 17], 3D EBSD (Electron Back Scattering Diffraction) [18-20], ECCI (Electron Channeling Contrast Imaging) [15, 21, 22], and micromechanical experiments under well-controlled boundary conditions [23-28].

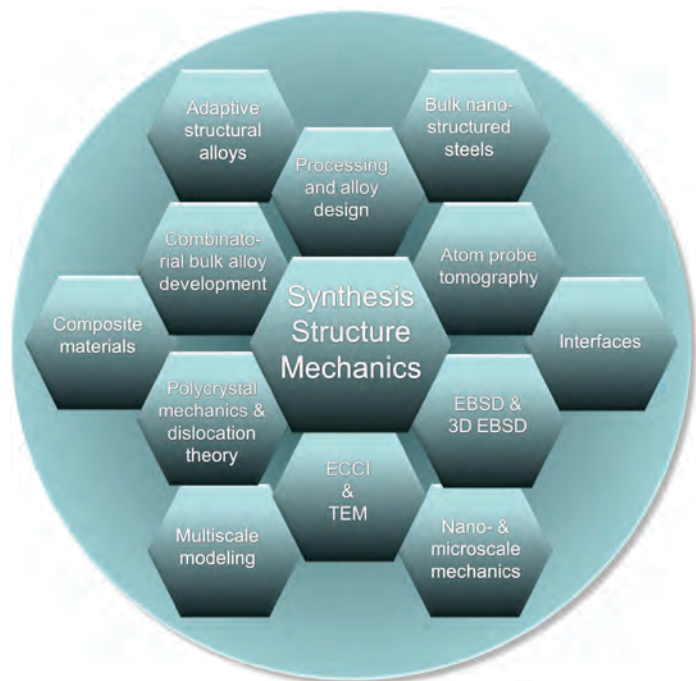


Fig. 1: Main research areas in the department.

Examples of simulation tools are defect-based constitutive models of microstructure evolution and microstructure-property relations at different length scales such as crystal plasticity spectral and finite element solvers [16, 23, 25, 26, 28-34] or discrete dislocation dynamics [35, 36]. Close interfacing of simulation and experiment with the aim to quantitatively compare the two has high priority [4, 8, 16]. Since microstructures of engineering alloys are typically designed by imposing a sequence of thermo-mechanical treatments, the effects of synthesis and processing on the microstructure evolution and hence on the mechanical response of the materials increasingly gains momentum in our projects. Examples are the development of a new class

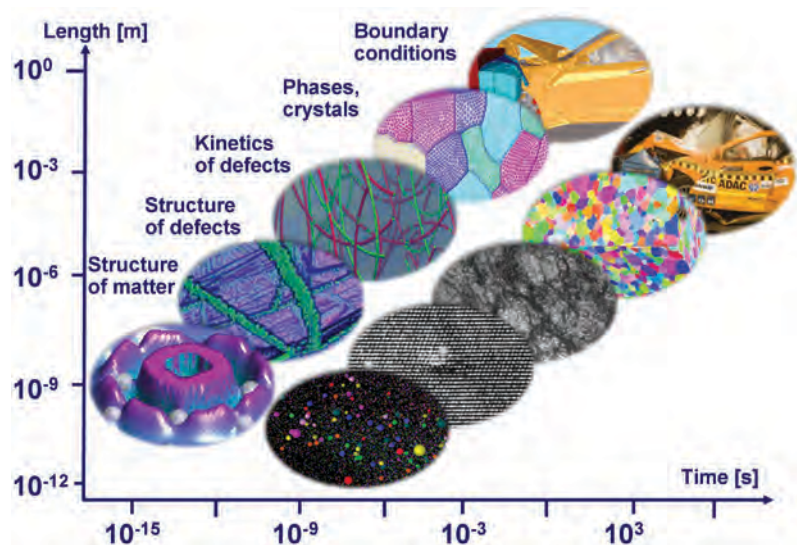


Fig. 2: Scales in computational materials mechanics and how they match corresponding experiments. Here we show the specific example of crystal plasticity.

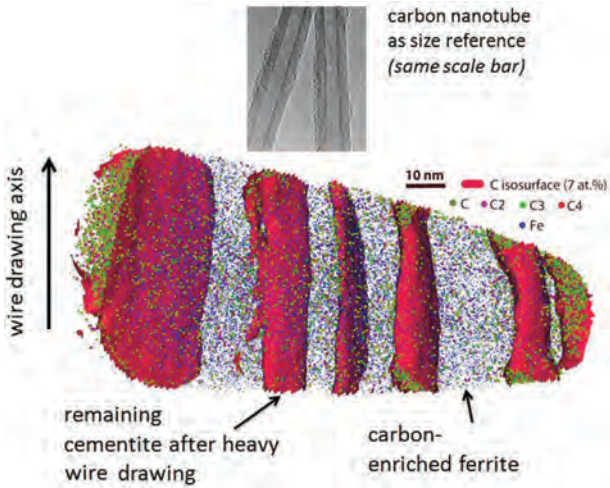


Fig. 3: Heavily deformed pearlite is characterized by ferrite-cementite nanostructures with dimensions that are as fine as those of carbon nanotubes (Y.J. Li, S. Goto, R. Kirchheim) [41-43].

of ductile, damage-tolerant maraging-TRIP steels by nanoscale precipitation of intermetallic phases and re-austenitization at interfaces [1,37,38].

Recent strategic scientific developments in the department were the opening of a new group on Atom Probe Tomography (APT) in 2010 [1,5,11,14]; the close collaboration with the department of J. Neugebauer on multiscale modeling of hardening and phase transformation phenomena as well as on computational thermodynamics [2-4,8]; and the strengthening of our metallurgical synthesis competence bundled in a new group on 'Combinatorial Metallurgy and Processing' that was opened in 2012 [39] (see p. 15).

The ability to probe the chemical and structural state of complex lattice defects (e.g. grain boundary segregation and nano-precipitates in Mn-steels [1] and pearlite [17,41-43] (see p. 107) by high resolution experiments (APT, TEM) does not only enable the direct comparison between experiments and atomistic simulations but it also opens a new pathway towards the atomic-scale characterization of lattice defects in functional materials. Examples are the chemical characterization of quantum-wells in LEDs [10], of decorated grain boundaries in CIGS and Si solar cells [11], and of nano-particles in soft magnetic alloys. In all these materials near-atomic characterization of defects is essential for understanding functional structure-property relations.

Projects demonstrating the strong inter-departmental links in the field of multiscale modelling are the *ab initio* prediction of phase stability and interface energies in complex steels (see p. 101), the *ab initio* guided development of

ductile Mg alloys (p. 111), and Ti-based instable BCC and related Gum alloys which are characterized by large plastic yet hardening-free deformations (p. 113).

A further important step was the start of a new research group in 2012 on combinatorial metallurgy and processing (H. Springer) (see p. 15) [39]. This group conducts interdisciplinary research on alloy design and joining [40] of complex structural materials. We pursue a variety of new metallurgical synthesis methods, such as strip casting, amorphous steel solidification and specifically a new combinatorial high throughput approach that is specifically suited to systematically explore wide composition and property regimes of novel bulk structural alloys ('steel plant in a box') [39]. For this purpose we render the well-established combinatorial thin-layer approach into larger bulk quantities (kg-scale) and include – besides the variation in composition – also solidification, thermomechanical treatment, forming, and welding parameters. The aim is to probe large phase spaces of complex alloys under consideration of the required process parameters.

Close cooperation of the department exists with the institute's external scientific member R. Kirchheim on the fundamentals of the strength of heavily deformed Fe-C systems (see p. 107). This collaboration aims at a better understanding of the origin of deformation-induced alloying and the associated stabilization of sub-grain nanostructures via defectant effects, Fig. 3 [17,41-43]. Similarly, we closely cooperate with the Max-Planck Fellow G. Eggeler on elementary dislocation creep processes in high temperature alloys, Fig. 4.

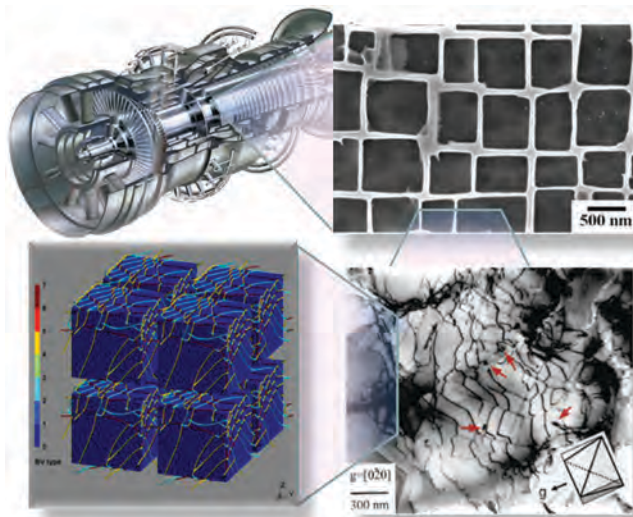


Fig. 4: Scale-bridging analysis of the structure of Ni-base superalloys. Elementary dislocation kinetics and reaction rates during primary, secondary, and tertiary creep can be simulated using discrete dislocation dynamics (DDD) (B. Liu, A. Kostka, G. Eggeler).



Scientific Groups

Introduction

The department has five permanent scientific groups,

- Theory and Simulation (F. Roters)
- Diffraction and Microscopy (S. Zaefferer)
- Alloy Design and Thermomechanical Processing (D. Ponge)
- Biological Materials (H. Fabritius)
- Combinatorial Metallurgy and Processing (H. Springer)

and five additional non-permanent scientific groups financed by third-party funds,

- Atom Probe Tomography (P. Choi, funded by Leibniz award)
- Adaptive Structural Materials (C. Tasan and B Grabowski, funded by ERC advanced grant)
- Computational Mechanics of Polycrystals (P. Eisenlohr, funded by MPG-FhG program of Max-Planck-Society)
- Theory and Simulation of Complex Fluids (F. Varnik, funded by MMM-initiative of Max-Planck-Society)
- Intermetallic Materials (F. Stein, M. Palm; group will be merged into new department of G. Dehm)

Owing to their extramural funding the latter initiatives are temporary groups. The project of P. Eisenlohr on the Computational Mechanics of Polycrystals was jointly funded after two subsequent evaluation workshops (2005, 2008) by the Max-Planck-Society and the Fraunhofer-Society for 3+3 years, 2005-2011. The group of F. Varnik on the Theory and Simulation of Complex Fluids was funded by the Max-Planck-Multiscale Modeling Initiative for 4 years, 2005-2009. Now it is carried further jointly through third party funds of MPIE and institutional funds of ICAMS (Interdisciplinary Centre for Advanced Materials Simulation) at Ruhr-University Bochum, Germany. The Atom Probe Tomography group, headed by P. Choi, has been established in 2010. It is financed through Prof. Raabe's Leibniz Award (German Research Foundation, DFG). The group for Adaptive Structural Materials, headed jointly by C. Tasan and B. Grabowski, is funded by an ERC advanced grant that was awarded in 2012 to D. Raabe and J. Neugebauer. The group for Intermetallic Materials was originally part of the department of the late Prof. Frommeyer and is currently cooperating with us on high temperature materials, iron-aluminides, and Laves phases. Since October 2012 it belongs to the new department of G. Dehm.

Research Focus of Permanent Groups

Theory and Simulation (F. Roters)

Group Mission. The group develops mechanism-based **crystal plasticity** constitutive models that describe the relationship between microstructures and mechanical properties of crystalline materials [16]. The approaches are based on mean-field formulations that describe the evolution of lattice defect structure such as dislocations and twins under given mechanical or thermal loading boundary conditions. The predicted defect densities enter into kinetic structure-property relations that translate them into strength and deformation measures [44,45]. Owing to the crystalline anisotropy of metallic alloys the constitutive laws assume a tensorial form both in their elastic and plastic formulations, i.e. they predict the defect evolutions on all crystallographic shear and twinning systems under external loads and their internal interactions. The formulations are built on dislocation densities (different types depending on the exact model), and can include mechanical twinning as additional deformation carrier. Interactions among dislocations and of dislocations with twins and grain boundaries can be considered. The resulting sets of nonlinear internal-variable differential equations are solved using either the **Finite Element Method** (CPFEM) [16,19,25,26,29,32-34,47,48] or a **Spectral Method** (CPFEM) [49,50], Fig. 5.

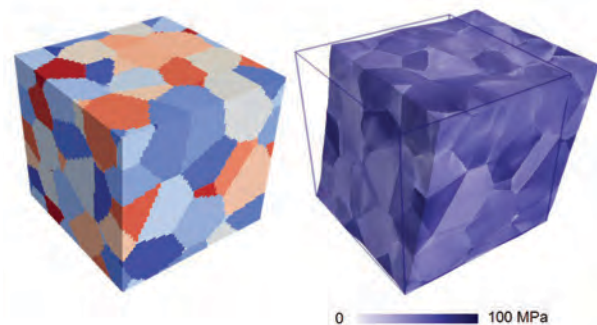


Fig. 5: Simulation of simple shear using the spectral solver; left: volume element with periodic boundaries containing 50 grains with random orientation; 256x256x256 grid points; right: yz-component of first Piola-Kirchhoff stress after 20 % yz-shear deformation (F. Roters, M. Diehl, P. Eisenlohr, R. Lebensohn).

Research Highlights 2010-2012 including main trends over the past 6 years. The most important highlight during the past years was the further development of a Spectral Crystal Plasticity (Fast Fourier) Method (**CPFEM**) together with R. Lebensohn from Los Alamos who spent a year in the group as Alexander von Humboldt Awardee [49,50]. This method was modified to enable the use of advanced non-linear constitutive models, such as described above, and equipped with

a robust integration algorithm. Furthermore, a regrinding capability has been developed to ensure that the gradual micromechanical distortions do not impede convergence. The fundamental advantage of this approach is that FFTs can solve the underlying constitutive elasto-plastic equations under periodic boundary conditions about orders of magnitude faster than FEM solvers at much lower memory costs. Also CPFEM has the advantage that it can directly be applied to EBSD or other fixed-grid microstructure data sets circumventing the requirement to reconstruct complicated mesh geometries as it should be done for corresponding CPFEM simulations. The novel method is mature and currently successfully applied to full-field simulations of deformation heterogeneity in dual phase steels, porous alloys, and ice mechanics.

Another field of activity was the application of advanced CPFEM simulations to the prediction and better understanding of shear banding in crystalline materials [16]. Shear bands are the most frequently observed yet least understood mesoscopic, collective plasticity mechanism. They play an essential role in strain hardening, strain localization, texture evolution, and damage initiation. We found that shear banding is strongly orientation dependent. For example Copper and Brass-R-oriented crystals (FCC lattice) show the largest tendency to form shear bands and build up an inhomogeneous texture inside the shear bands. Shear banding in these crystals can be understood in terms of a mesoscopic softening mechanism. The predicted local textures and the shear banding patterns agree well with experimental observations in low SFE FCC crystals [47,48].

The progress in these various fields of polycrystal mechanical modeling achieved by our group in terms of methods development and applications was recently published as an overview article in *Acta Materialia* [16] and is since its appearance the most downloaded publication of all papers published in this journal. The software developed during the last years was released to the public domain as Düsseldorf Advanced Materials Simulation Kit (DAMASK) and can be downloaded from the internet: <http://damask.mpie.de>. It is already used by several research groups in Europe and the US.

Another growing field of interest are **discrete dislocation dynamics** (DDD) simulations [35,36]. These models are built on three assumptions. First, the distortions around lattice dislocations are treated as linear elastic fields and are solved piecewise (i.e. for a portion of the dislocation) via the Volterra equation and Hooke's law. Second, all dislocation lines are decomposed into sequences of connected segments. Third, the dynamics of each segment is solved using a damped viscous form of the equation of motion considering long and short range elastic interactions among all dislocation segments via the Peach-Koehler equation plus external loads. The simulations using the massively parallel ParaDiS

code of the Lawrence Livermore National Laboratory (USA) [51] are computationally highly demanding so that they run on the Blue Gene/P high performance computer of FZ Jülich on up to several thousand processors.

In this field we also aim twofold: First we improve the theoretical foundations of the approach further (e.g. by including dislocation climb) and second apply it to problems where the simulation of small sets of interacting dislocations provides insights into the underlying micromechanics.

Main projects pursued by discrete dislocation simulations are the strengthening effects of small angle grain boundaries [35,36], creep in Ni-based superalloys (Fig. 4), and dislocation patterning.

Microscopy and Diffraction (S. Zaefferer)

Group Mission. The group pursues two main missions. The first one is the development of advanced microstructure characterization methods focussing during the past years on SEM- and FIB-SEM based approaches. Specific focus is placed on diffraction methods such as high angular and spatial resolution orientation microscopy (**HR EBSD**) in the SEM, **electron channelling contrast imaging** (ECCI), **internal stress** determination via SEM/EBSD, and 3D electron backscatter diffraction (**3D EBSD**, tomographic EBSD) [6,15,18-22,55-57].

The second main objective of the group lies in the application of these advanced characterization methods with the aim to understand and quantify with high crystallographic precision microstructure evolution phenomena associated with transformation and plasticity mechanisms and the proper characterization of the dislocations and interfaces involved. The metallurgical phenomena of interest are mainly in the fields of polycrystal crystal plasticity (mainly steels, Ni-alloys, and Mg-alloys), twinning and martensitic transformation (in steels with twinning or transformation induced plasticity (TWIP or TRIP)) as well as annealing phenomena.

The group operates several instruments. Among these is a Zeiss Crossbeam XB1560 FIB-SEM for 3D EBSD investigations, a JEOL JSM 6500 F SEM (both with field emission gun), and a Camscan 4 tungsten filament SEM. These instruments are equipped with EBSD analysis hardware and allow mounting micro-deformation machines for *in situ* deformation testing. A heating stage is also available for conducting *in situ* transformation experiments. For ECCI a eucentric 5-axis goniometer stage has been custom-designed by Kleindiek nanotechnology. Transmission electron microscopy (TEM) is performed on a Phillips CM 20. This instrument is equipped with a large angle, high dynamics camera (Olympus) for image and diffraction pattern acquisition and the software TOCA for on-line crystallographic analysis. Furthermore, several XRD goniometers are available.

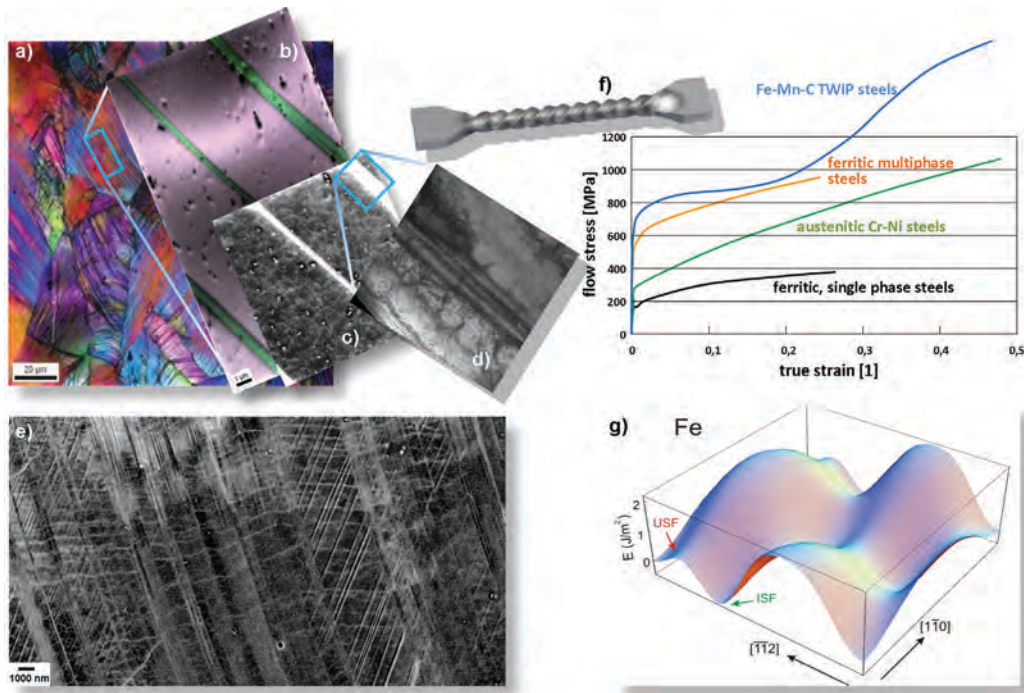


Fig. 6: Example of a Fe-Mn TWIP steel (22 wt.% Mn, 0.6 wt.% C) where an instability analysis (in terms of the stacking fault energy) is used to design the desired transformation behaviour (here: evolution of twins during deformation). The result is a strong increase in both, strength and ductility. Slight changes in the chemical composition modify the stability of the FCC Fe-Mn-C matrix against mechanical twinning and can shift the system towards preferring other transformations (e.g. ϵ -martensite, tetragonal martensite). The images on the left and side reveal the hierarchical microstructure after an equivalent strain of about 20% which can – irrespective of its enormous complexity – be understood in terms of the stacking fault energy. The images on the left hand side are obtained via a) EBSD (electron back scatter diffraction) image; b) high resolution EBSD; c) ECCI (electron channelling contrast imaging) revealing also dislocations (see also wide-field of view ECCI micrograph (e) at the bottom); and d) TEM (transmission electron microscopy). The right hand side shows the enormous increase in the strength-ductility profile of this novel alloy compared to conventional materials that are plotted in the same diagram. The results of the *ab initio* prediction of the generalized γ -surface (by department of J. Neugebauer) is shown in g) and allows to extract critical information such as the intrinsic stacking fault (ISF) energy or its kinetic barrier to create it (unstable stacking fault – USF) energy (I. Gutierrez-Urrutia, J. Neugebauer).

Research Highlights 2010-2012 including main trends over the past 6 years. Highlight activities of the group during the past two years were the development of a new approach to electron channelling contrast imaging (ECCI), named “controlled ECCI”, or cECCI [15,21,22], Fig. 6. This method improves the existing ECCI method in a way that it uses EBSD to determine the crystal orientation. Based on this the optimum sample alignment for

obtaining good channelling contrast is calculated using the computer software TOCA [52]. A dedicated eucentric goniometer stage is then used to move the sample into the calculated position for imaging of dislocations and other crystal defects in the SEM. The approach offers excellent opportunities for the efficient quantification of substructure features at a large field of view that were not accessible so far to SEM characterization, Fig. 7. It can be combined with

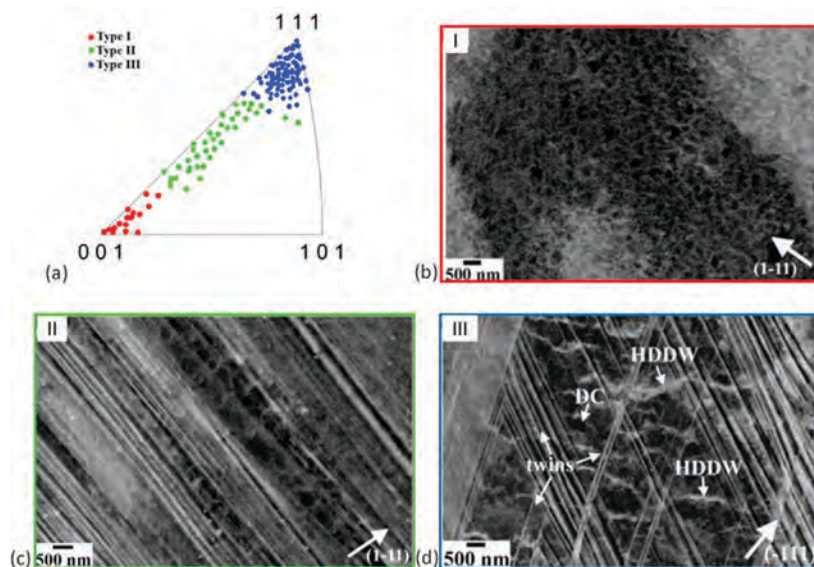


Fig. 7: Different deformation structures observed with controlled electron channelling contrast imaging (cECCI) in a TWIP steel deformed in a tensile test to a true strain of 0.3. (a) Standard orientation triangle indicating the tensile direction in crystal coordinates for different crystals in the material. Crystals with different characteristic deformation structures are classified as type I, II and III. (b) Dislocation cell structure typical for grains of type I. (c) Dense single system twin lamellae, typical for grains of type II. (d) Several twin systems, typical for grains of type III (from [21]). DC: dislocation cell, HDDW: highly dense dislocation walls.

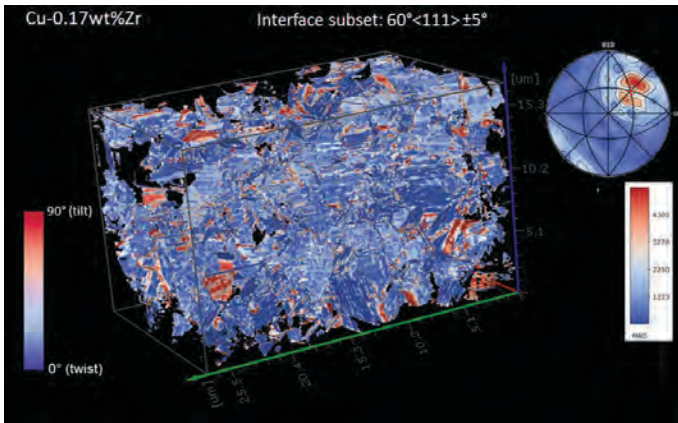


Fig. 8: Characterization of the tilt and twist fractions of the $60^\circ \langle 111 \rangle$ grain boundary family in a deformed Cu-Zr sample by 3D EBSD (P.J. Konijnenberg).

capable of conducting detailed microstructure quantification mappings of orientations together with its inherent dislocation substructure in the same experiment. Tedious and time consuming TEM investigations of dislocation structures that provide a small field of view thus may become obsolete in a number of cases.

A second focus of the group lies in the improved analysis of 3D EBSD data with respect to the characterisation of interface segments. As was shown in the last bi-annual reports it is in principle straight forward to extend the 2D EBSD (electron backscatter diffraction)-based orientation microscopy technique to a 3D technique by collecting sequential sets of 2D maps by serial sectioning, e.g. by mechanical or chemical polishing or sputtering with a focussed ion beam (FIB). 3D EBSD offers unique and novel features to characterize microstructures, in particular the full, 5-parameter grain boundary description but also, for example, the description of connectivity of phases, 3D morphology of crystals, or the determination of geometrically necessary dislocation (GND) densities [20,33]. The 3D EBSD data can be analysed in two approaches, either as volume pixels (voxels) or by rendering interfaces and boundaries. While the former method has been discussed in the past reports the interface segment reconstruction is currently the most important pending problem. In our current approach the grain boundary reconstruction consists of two sequential steps; namely, first, in identifying the boundary surface and subsequently translating this surface into a mesh of triangles. A well-known method for boundary reconstruction is the Marching Cubes (MC) algorithm which has been applied for boundary reconstruction from orientation voxels before. The standard MC algorithm suffers from several inherent ambiguities. These ambiguities can be solved by disassembling each cube into unambiguous tetrahedra, resulting in the so-called Marching Tetrahedra (MT) algorithm which leads to better results. Once grain boundaries are established as sets of triangles these boundaries have to be smoothed before any quantitative statements about

spatial or crystallographic features of the boundaries can be made. Different smoothing algorithms have been developed and tested. Furthermore a number of algorithms have been developed to display and interpret the crystallographic nature of boundaries in the 5 parameter grain boundary space (3 parameters describing the misorientation and 2 the boundary normal) [53], Fig. 8.

The algorithms used for interface characterization are part of a large software suite, Qube, which has been developed over the last two years mainly by P. Konijnenberg. It embeds under a user-friendly software interface powerful tools for 3D microstructure characterization. This includes, for example, the calculation of GND densities from the 3D orientation field curvature, the calculation of 3D orientation gradients, 3D rendering of interfaces and the quantitative calculation of grain and boundary textures (see p. 117).

A further recent focus of the group is placed on the development and use of EBSD-based methods for the measurement of local elastic (lattice) and plastic strain. In one approach, followed by T. Jaepel, a cross-correlation technique is used to measure the distribution of lattice strains inside of individual crystals of a polycrystal or in single crystal samples. The fact that this technique requires reference patterns of similar orientation limits this technique to special cases and does not allow determining absolute levels of internal stresses. A second approach, therefore, uses a reference pattern-free algorithm to measure absolute lattice strains. A third approach, finally, is followed by F. Ram, who developed the Kikuchi bandlet method to determine with highest accuracy the position of Kikuchi cones from EBSD patterns. These data can then be used to determine the geometrical pattern origin and the lattice distortion with high accuracy. The Kikuchi bandlet method can also be used to determine, from the Kikuchi band profile, the crystal defect density (i.e. the total dislocation density) in the electron beam interaction volume.

Related to the measurements of stress and strain are research initiatives which use *in situ* deformation tests to observe strain hardening mechanisms in various materials. Besides local strain measurements with the above mentioned techniques these projects use ECCI and digital image correlation to quantify the local plastic strain. The project is pursued by C. Tasan.

Finally, several research initiatives deal with the statistical representativeness of local property measurements. In a project on low alloyed TRIP steels the statistical representativeness of EBSD for phase and texture determination was studied and a new software tool for large area measurements

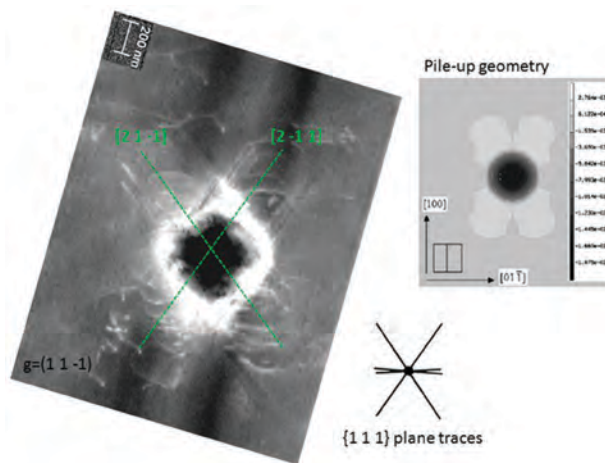


Fig. 9: Dislocation structure around a nanoindent on an undeformed TWIP steel surface observed by cECCI. Dislocations are emitted out of the nanoindent in $\langle 112 \rangle$ directions. This corresponds to the expected pile-up symmetry displayed on the right side calculated by crystal plasticity FEM (J. Zhang).

developed [54]. Another project, pursued so far by J. Zhang, deals with the analysis of nanoindentation for measurement of residual stresses. The results are interpreted in terms of dislocation structures that are observed using the cECCI technique, Fig. 9.

Alloy Design and Thermomechanical Processing (D. Ponge)

Group Mission. In the past 6 years the group worked mainly on microstructure design and optimization of the mechanical properties of carbon-manganese steels via grain refinement by thermomechanical treatment [55,58-63]. Main examples were the design of advanced ultrastrong spring steels and bulk ultra-fine grain steels. More specific the main alloy systems addressed were ultra fine grained plain C-Mn steels and dual phase (DP) steels for light-weight automotive applications [55, 58-63]. The microstructure-oriented optimization of microstructures and properties of novel complex engineering steels via thermomechanical treatment requires a detailed understanding of the relations between processing and microstructure evolution on the one hand and the relations between microstructures and mechanical properties on the other. This two-fold strategy is essential in this field as no direct link exists between processing and properties.

In addition to the development of optimal thermomechanical processes, in the past few years projects increasingly included mechanism-based alloy design strategies [1,15,21,22,64,65]. The reason is that alloy development is an ideal addition to thermomechanical processing as it gives access to a larger variety of bulk phase transformations, precipitate strategies, and grain refinement mechanisms. The joint design of both, novel alloy variants

in accord with thermodynamic and kinetic prediction tools and adequate thermomechanical processing hence describes the current research strategy of the group (see p. 101). In order to probe the composition phase space more efficiently the team closely interacts with the new group on combinatorial metallurgy and processing (see p. 15).

Research Highlights 2010-2012 including main trends over the past 6 years. During the past two years the group was mainly concerned with the development of a new alloy class, namely, Mn-based lean maraging-TRIP steels [1,37,38]. The concept is based on combining the TRIP effect with the maraging effect (TRIP: transformation-induced plasticity; maraging: martensite aging) (see p. 101). The Fe-Mn-based maraging-TRIP alloys combine different hardening mechanisms. The first one is the formation of strain-induced martensite (alloys with 0.01 wt.% C and 12 wt.% Mn have retained austenite fractions up to 15 vol.%) and exploits the same hardening principles as TRIP steels. The second effect is the strain hardening of the already transformed ductile, low carbon α' - and ϵ -martensite phases and of the remaining retained austenite. The third effect is the formation of nano-sized intermetallic precipitates in the martensite during heat treatment. These precipitates have high dispersion owing to the good nucleation conditions in the heavily strained martensite matrix in which they form. The fourth one is the formation of nanoscaled re-austenitization layers on the formerly segregation-decorated martensite grain boundaries during the maraging heat treatment. This combination of mechanisms leads to the surprising property that both strength and total elongation jointly increase upon martensite aging (e.g. 450°C, 48 hours) reaching an ultimate tensile strength of nearly 1.3 GPa at an elongation above 20% [37,38].

Specifically the occurrence of nano-scaled re-austenitization layers at the martensite grain boundaries seems to have a beneficial effect on the blunting of cracks rendering the martensite ductile. This effect could be realized in a second alloy class, namely, in a martensitic Fe-13.6 Cr-0.44 C (wt.%) martensite steel. After tempering the martensite was rendered into an ultra-high-strength ferritic stainless steel with excellent ductility. The nanoscale austenite reversion mechanism that occurred in this alloy is coupled to the kinetic freezing of carbon during low-temperature partitioning at the interfaces between martensite and retained austenite and to carbon segregation at martensite-martensite grain boundaries. An advantage of austenite reversion is its scalability, i.e. changing tempering time and temperature tailors the desired strength-ductility profiles. E.g. tempering at 400 °C for 1 min produces a 2 GPa ultimate tensile strength (UTS) and 14% elongation while 30 min at 400 °C results in a UTS of 1.75 GPa with an elongation of 23% [14].

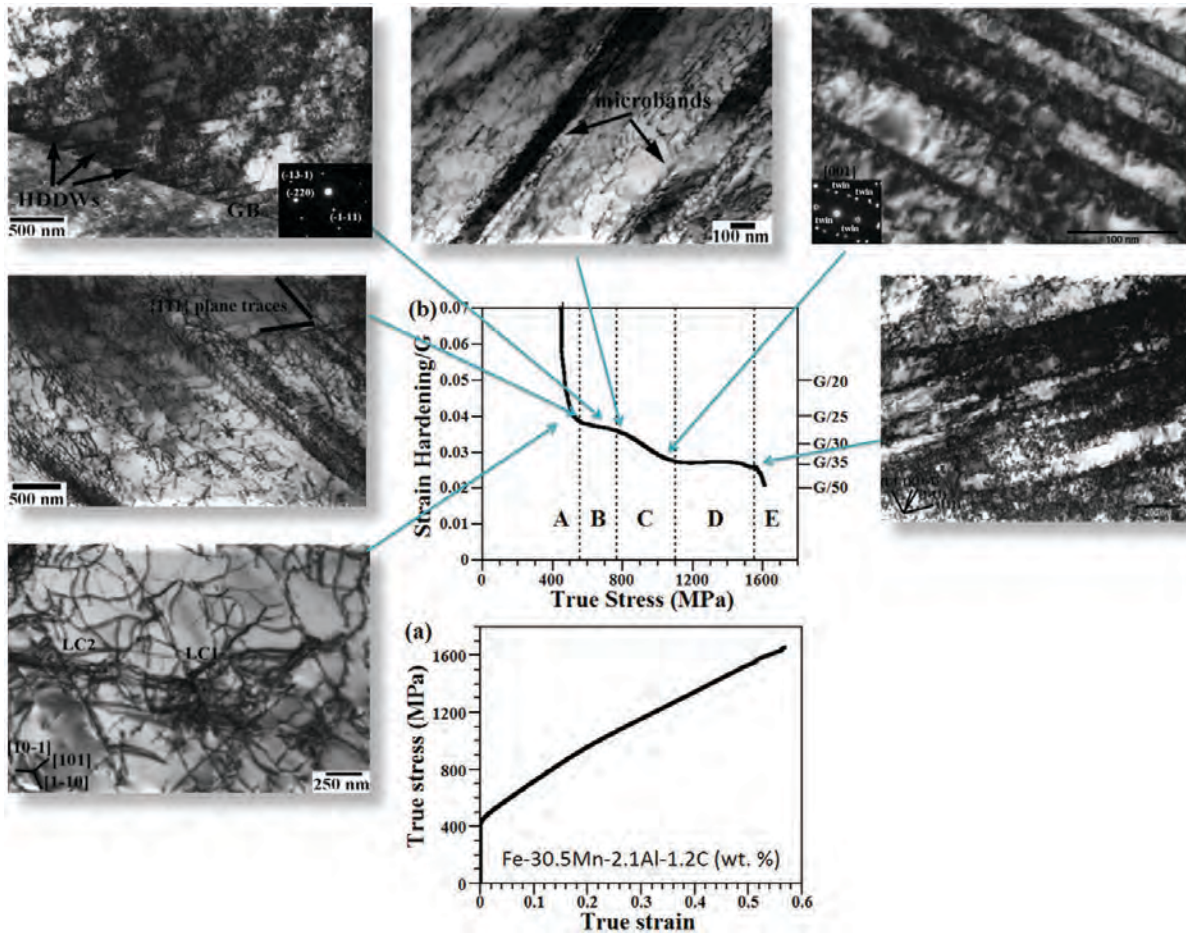


Fig. 10: Non-heat treated Fe–30.5Mn–2.1Al–1.2C (wt.%) weight-reduced steel with fcc crystal structure. Characterization of the different strain hardening stages using TEM analysis (I. Gutierrez-Urrutia) [15].

A third group of steels that is being addressed jointly by this group and the new group on combinatorial alloy design are weight-reduced austenitic or austenitic-ferritic steels. These are steels with up to 30 wt.% Mn, up to 8 wt.% Al and up to 1.2 wt.% C which are sometimes also referred to as TRIPLEX steels owing to their two- or three phase composition. They are characterized by about 10% reduced specific weight and excellent stress-ductility profiles, Fig. 10. Depending on heat treatment and composition they can contain nanostructured kappa carbides [39].

Biological Materials (H. Fabritius)

Group Mission. Most biological materials with structural functions consist of an organic matrix of structural biopolymers like collagen and chitin, which is modified and reinforced with different proteins and in many cases also with biominerals. The most prominent examples like the bones of vertebrates, the exoskeletons of arthropods, and mollusk shells are known to possess optimized function-related physical properties (e.g., mechanical properties: stiffness-to-density ratio and fracture toughness). The origins of these properties, particularly the underlying structure/composition/property relations, are the research subject of this group [66-70].

In our work on mineralized chitin-based arthropod cuticle we found out that the specific design and properties at the nanoscale contribute significantly to their macroscopic properties. Evidently, the overall properties depend on the specific microstructure at all levels of hierarchy [8,71]. However, especially the properties at small length scales are experimentally hard, if not impossible, to access due to methodological constraints. Hence, multiscale modeling that can systematically describe and investigate materials properties from the atomistic scale up to the macroscopic level has become a major approach in the group in close cooperation with the department of J. Neugebauer to tackle the structure/property relations of biological organic/inorganic nanocomposites. The method has been applied to bone and crustacean cuticle [8,72,73]. In addition to modeling fully differentiated structural composites, the approach has also been applied to model the mechanical properties of individual constituents and explain the structure/property relations on increasingly complex structural hierarchy levels.

Research Highlights 2010-2012 including main trends over the past 6 years. The cuticle of *Arthropoda* is a continuous tissue that covers the entire body. In order to function as an exoskeleton, it



has to form skeletal elements with physical properties that are adapted to specific functions which are very diverse, like providing mechanical stability in the shell of body segments, elasticity in arthroal membranes, or wear resistance and friction reduction in joint structures and mandibles. The required properties for each skeletal element are adjusted by local modifications in structure and composition. The transitions between parts with different properties are brought about by structural interfaces, which are generated on different hierarchical levels. Employing our established experimental approaches, we investigate the nature of such interfaces in functionally differentiated cuticle parts such as mandibles of *Crustacea* species with different feeding habits and transitions between mineralized load-bearing cuticle and unmineralized arthroal membranes. Since our theoretical multi-scale model can only predict the average elastic properties of cuticle, we developed a hierarchical model for the elasto-viscoplastic cuticle properties at large deformations using a Fast Fourier Transforms (FFT) approach that is able to describe the local development of stress and strain fields within the material, including those at the interfaces.

In addition to serving as exoskeleton, the cuticle of *Arthropoda* also plays an important role for the ecophysiology of the organisms by forming photonic crystals that generate colors through scattering of light by photonic band gap materials. We use the cuticle of various beetle species to both experimentally and theoretically investigate the structure and resulting optical properties of photonic crystals as found in the small scales covering the beetle *Entimus imperialis*. They consist of a diamond-structured cuticular network and air, where the structural parameters are optimized to produce the brightest colors possible by maximizing band gaps width. In some scales, this effect is turned into the opposite, transparency, through alteration of the refractive index contrast by substitution of the air with SiO_2 . In collaboration with the group of Prof. Zollfrank (TU Munich), this biological photonic crystal has been biomimetically transferred into identical silica replicas with tunable structural parameters. Based on these results, we started to combine experiments and theory to develop biomimetic photonic crystals with tailored optical and mechanical properties for potential mechanochromic applications (see p. 139).

Over the last years, we expanded our studies on structure/property relations in biological composites beyond mechanical properties with particular focus on multifunctional parts, property transitions and different and/or unusual property combinations with the aim to expand the knowledge necessary to develop corresponding synthetic materials.

Combinatorial Metallurgy and Processing (H. Springer)

See separate presentation of this new initiative on page 15.

Overview on Non-Permanent Groups and Their Research Focus in the Past Years

Atom Probe Tomography (P. Choi, funded by Leibniz award)

Group Mission. The group was opened in 2010 and has since then seen very rapid growth in terms of topics and personnel. Atom Probe Tomography (APT) is a characterization technique enabling spatially resolved chemical analyses of materials at sub-nanometer resolution (in-plane: ≈ 0.2 nm; in-depth: ≈ 0.1 nm) [1,9,11,14,17,41-43]. The instrument (Imago Scientific Instruments, LEAP 3000X HR) is equipped with a local electrode, a wide-angle reflectron, a high-speed delay line detector system as well as an ultrafast laser with a pulse width of 10 ps and wavelength of 510 nm. Such an instrument design has numerous advantages over conventional atom probes, particularly regarding the analysis of alloys with complex chemical composition. The local electrode enhances the electric field at the specimen and allows fast pulsing (max. 200 kHz) at low voltage. A high-speed delay line detector system provides fast data acquisition rates of up to 2 Mio ions/min. Due to the proximity between specimen and detector, the field of view can be as large as 200 nm. As a result, large volumes, which can contain up to several hundred millions of atoms, can be probed within a few hours. The wide-angle reflectron substantially enhances the mass resolution of this instrument. Complex multi-component systems can therefore be analyzed at high compositional accuracy. Furthermore, impurity concentrations as low as few tens of ppm can be detected. The ultrafast laser extends the applicability of this technique to materials having low electrical conductivity such as semiconductors and ceramics [10,11].

The research objectives of the group are in two fields. The first one is the near-atomic scale analysis of interface-related phenomena, such as segregation, partitioning and associated local thermodynamic and kinetic phenomena, for instance phase transformations at grain boundaries [1,14]. Owing to the capability of instrument to probe samples with small electrical conductive in Laser excitation mode, increasingly also interfaces and quantum well structures of functional polycrystalline materials are studied.

The second aim of the group lies in comparing atom probe tomography observations quantitatively with theoretical predictions. For this purpose we use ThermoCalc and Dictra approaches as well as *ab initio* predictions in conjunction with kinetic Monte Carlo methods. While the former set of statistical simulations are mainly conducted in close collaboration with G. Inden and the group of D. Ponge

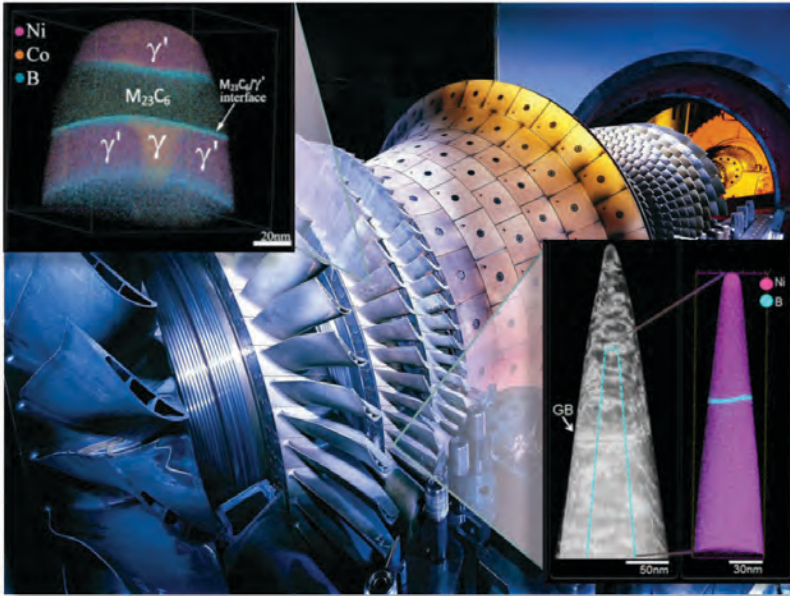


Fig. 11: Use of atom probe tomography for the analysis of the atomistic details of carbide formation and boron-decoration of interfaces in Ni-base alloys that are developed as blade components for power plant turbines (D. Tytko, I. Povstugar) [5].

(Alloy Design and Thermomechanical Processing) the latter calculations are done in the department of J. Neugebauer in the group of T. Hickel (Computational Phase Studies).

Research Highlights 2010-2012 including main trends over the past 3 years. The group studies both, functional and structural materials. Examples are thin-film solar cells (based on Cu(In,Ga)Se₂ and CdTe) and light-emitting diodes (based on III-V semiconductors) [10], as well as Al- and Cr-Nitride multilayer hardcoatings. Regarding metallic alloys essential research topics are the formation of nanoscaled re-austenitization films on martensite grain boundaries in Fe-Cr-C and Fe-Mn steels; interfaces in Ni-based superalloys, Fig. 11 [5]; the stabilization of ferrite nanograins in mechanically alloyed and heavily deformed pearlite by massive carbon decoration of the grain boundaries [41-43]; the formation of Cu-based nano-precipitates in Fe-Si-Cu soft magnetic steels; partially crystalline soft magnetic metallic glasses; and nano-structured carbides in weight reduced Fe-Mn-Al-C steels, Fig. 12. The group is currently financed through the funds of Prof. Raabe's Leibniz Award (German Research Foundation, DFG).

Adaptive Structural Materials (C. Tasan and B. Grabowski, funded by ERC advanced grant)

See separate presentation of this new initiative on page 13.

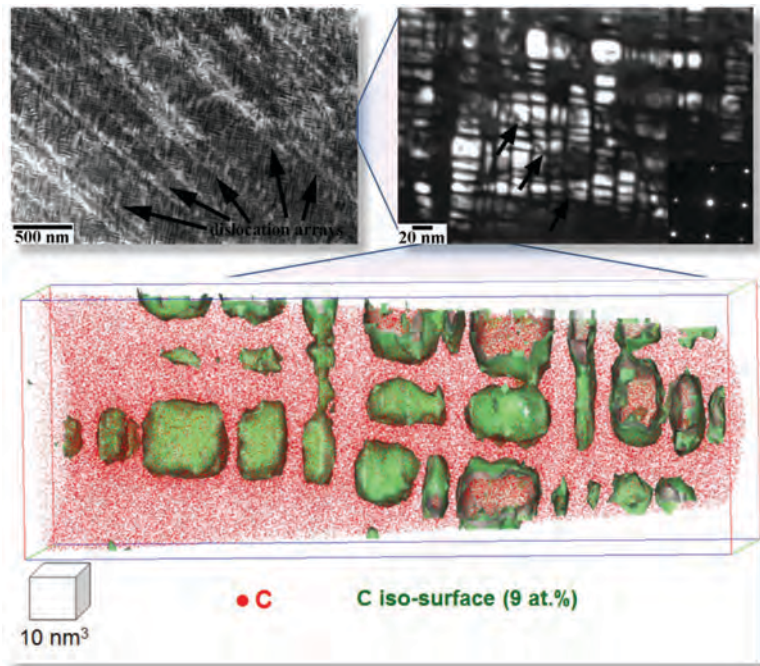


Fig. 12: Formation of nano-sized kappa-carbides in weight-reduced Fe-Mn-Al-C steel using ECCI, TEM, and APT (J. Seol, P.-P. Choi, I. Gutierrez-Urrutia).

Max-Planck-Fraunhofer Group on Computational Mechanics of Polycrystals (P. Eisenlohr)

Group Mission. The group was founded in 2005 as the first joint research group between the Max-Planck-Society and the Fraunhofer-Society (Fraunhofer-Institut für Werkstoffmechanik IWM, Freiburg). Funding was jointly provided by the Max-Planck and Fraunhofer-Societies. The group develops theoretical approaches for the mechanics and damage initiation of textured polycrystalline matter with the aim to promote its use for industrial applications such as encountered in the fields of metal forming and microstructure mechanics.



Research Highlights 2010-2012 including main trends over the past 6 years. In the past years the group has pursued the following goals in collaboration with the group for Theory and Simulation (F. Roters) [16,50,74,75]: The first direction was the development of an advanced homogenization schemes [77,78]. This model calculates the stress for a group of interacting crystals under an external given boundary condition considering internal relaxations among the abutting crystals. Such approaches allow polycrystal simulations at a scale above the full-field crystal plasticity finite element schemes. A novel approach, referred to as Relaxed Grain Cluster model (RGC), was developed and successfully applied to steels. This method does not only improve existing homogenization schemes for polycrystal mechanics but it can also be used as a homogenization method for multiphase polycrystalline materials, such as for instance for TRIP steels.

The second aim of the group was the development of advanced constitutive models that describe the individual deformation behaviour inside the crystals. Of particular interest was the development of constitutive models that include deformation twinning and its interaction with dislocation slip [44]. Also, an improved mean-field dislocation flux model is being developed that communicates dislocation streams and balances reaction as well as annihilation rates among neighboring field integration points according to the local boundary conditions. This flux formulation accounts for geometrically necessary dislocations and the associated local stress peaks.

The third field is the role of heterogeneous deformation on damage nucleation at grain boundaries in single phase metals [26]. This work is done in close cooperation between our department (P. Eisenlohr) and T.R. Bieler and M.A. Crimp from Michigan State University in East Lansing, USA, and Professor D.E. Mason from Albion College in Albion, USA. The project aims to understand which mechanical criteria determine where and why cracks or voids form in a strained polycrystal particularly at grain boundaries. This project is jointly funded by the US and German research foundations, NSF and DFG.

Theory and Simulation of Complex Fluids (F. Varnik)

Group Mission. The group for the simulation of complex fluids is rooted both at the ICAMS at Ruhr-University Bochum and at MPIE. Its field is the study of the structural and mechanical properties of complex multiphase and colloidal fluids [79-85]. Typically, fluids can be deformed already when being exposed to weak forces such as in the case of shear melting. This effect often goes along with a drop in shear viscosity upon increasing shear rate.

This phenomenon is referred to as shear thinning. The relation between the stress and deformation for a complex fluid is often non-linear. There is a wide field of applications of complex fluid mechanics, for instance in polymer processing, metallurgical processing [86,87], and biology [81,82]. As a modeling method we mainly use the lattice Boltzmann method (LBM) and multiphase variants thereof [62-68]. LBM is well suited for the numerical calculation of fluid flow, heat, and solute transport. Unlike Navier-Stokes solvers, the LBM mimics flows as collections of pseudo-particles that are represented by a velocity distribution function. These fluid portions reside and interact on the nodes of a grid. System dynamics emerge by the repeated application of local rules for the motion, collision, and re-distribution of the fluid particles. The method is an ideal approach for mesoscale and scale-bridging simulations owing to its computational efficiency and versatility in terms of constitutive description of its pseudo-particles. Also it can be efficiently cast into parallel codes. In particular, LBM exhibits good numerical stability for simulating complex fluids, such as multi-phase and multi-component flow phenomena under complicated boundary conditions. Since LBM describes fluid motion at the level of the distribution functions, it can be naturally coupled with related simulation techniques such as cellular automata or phase field models [86,87].

Research Highlights 2010-2012 including main trends over the past 6 years. The group investigates problems in micro-fluidics such as inhomogeneous diffusive broadening, droplet and contact dynamics on chemically and topographically patterned substrates as well as flow between topographically rough walls. On the nano-scale, on the other hand, the group focuses on the effects of thermal fluctuations on droplet dynamics. Furthermore, the group has also developed efficient parallel LBM variants that are recently particularly used for the study of blood flow mechanics [64,68]. These studies have proved very fruitful with a number of interesting observations as well as theoretical predictions, the latter being verified by independent computer simulations. To name just a few examples, we mention the observation of instantaneous droplet motion on a gradient of texture, and the discovery of new types of wetting states in the case of small droplets with a size comparable to the roughness scale [84].

Intermetallic Materials (F. Stein, M. Palm)

The group for Intermetallic Materials was initially part of the department of the late Prof. Frommeyer and is currently closely cooperating with us on high temperature materials and iron-aluminides. Since October 2012 it is part of the new department of G. Dehm (see p. 91).

Key Interdisciplinary Research Fields of the Department

The groups introduced above represent the main **competence centers** of the department. Our mission, however, aims beyond these fields, i.e. we additionally pursue a number of joint **grand challenges** tackling of which requires efficient bundling of these skills. Some cross-disciplinary and cross-departmental topics are described in the **research highlight** section. Here, we introduce some main inter-disciplinary research fields where the different groups team up and conduct long-term fundamental research. In the past years three main areas prevailed, namely:

- I. Designing intrinsically nanostructured metallic alloys
- II. Advanced characterization of complex materials
- III. Predictive and quantitative multiscale models

In the following we give a concise introduction into our respective approaches:

I. New materials: Mechanism-oriented design of intrinsically nanostructured metallic alloys

The design of advanced high strength and damage tolerant metallic alloys for energy, mobility, safety, health and infrastructure applications forms the engineering and manufacturing backbone of our modern society. Examples are creep-resistant steels and Ni-alloys [5] in power plants and plane turbines; ultrahigh strength steels [1,14,21,39,44], Ti-, and Mg-alloys for light-weight mobility and aerospace design [2,3]; metallic glasses for low-loss functional components; or biomedical Ti-implant alloys in aging societies [4].

Since the Bronze Age the design of novel metallic alloys was based on trial and error approaches, owing to the complexity of the physical and chemical mechanisms involved and the engineering boundary conditions imposed during synthesis and manufacturing. This traditional method has two shortcomings. First, current alloy design is not based on systematic design rules but on metallurgical experience alone. This renders the development of novel alloys inefficient. Second, the increase in strength via traditional hardening mechanisms such as solute solution, increase in dislocation density, or second phase precipitates, albeit leading to a high strength level, always causes a dramatic decrease in ductility, i.e., making the material brittle and much more susceptible for failure.

The joint research field of designing new metallic alloys aims at solving this inverse strength-ductility problem: The recent achievements in *ab initio* modeling and atomic scale characterization methods presented above and in some of the highlight papers

open a fundamentally new pathway to the systematic and knowledge-based design of next generation metallic alloys. The objective is to use these methods to identify and utilize strengthening mechanisms that enable us to overcome the inverse relationship between strength and ductility. The key idea to better reconcile high strength and high ductility is to incorporate second phases into bulk alloys that are close or even beyond their mechanical and thermodynamic stability limit. While this sounds at a first glance counterintuitive – in the end we aim at materials with superior mechanical stability – the well-controlled inclusion of topologically confined phases with reduced stability provides a method to stimulate finely dispersed deformation-driven displacive transformations. Optimizing the degree of instability, dispersion, and volume mismatch associated with transformations allows one to tailor compliant microstructures that reduce damage initiation. The novelty of the approach is that the transformation occurs only in regions with high local stress concentrations and, hence, acts as spatially localized self-organized repair mechanisms against localization softening and premature internal damage owing to its associated strain hardening and compressive stresses. This new principle of designing higher mechanical stability of metallic alloys by including instable phases carries the potential to deviate from the inverse strength-ductility principle that currently sets a limit to advanced engineering alloys.

The cornerstones for this systematic alloy design approach are a better understanding of the thermodynamics and kinetics of instable phases; the bulk combinatorial lean synthesis, processing, and probing of corresponding alloy classes; and the discovery of the governing strain hardening mechanisms and their interactions.

Regarding the first aspect, the use of novel theoretical tools such as *ab initio* simulations (department of J. Neugebauer) together with established thermodynamic and kinetic simulation tools such as **ThermoCalc** and **Dictra**, and the conjunction with local experimental analysis are conducted to discover composition and processing niches where phase instability can be exploited to lead to stronger and yet more ductile mechanical response. The second method, namely the combinatorial manufacturing of corresponding bulk specimens is described on p. 15. The third aspect, i.e. the understanding of new strain hardening effects requires the use of careful high resolution and at the same time wide field of view characterization methods such as the quantitative electron channelling contrast imaging, TEM, and atom probe tomography. Regarding the interplay of the thermodynamics of

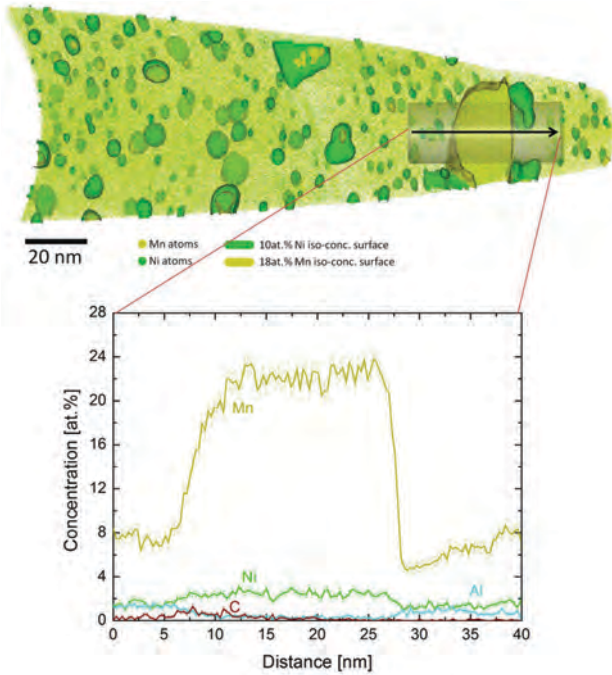


Fig. 13: APT observation of the formation of Mn-rich austenite at a martensite interface in a Fe-Mn-based maraging steel (Fe-12Mn-2Ni-0.15Al-1Ti-1Mo-0.01C, wt.%) upon quenching and subsequent tempering at 450°C for 48 hours. The in-grain envelope zones in the APT map indicate intermetallic nanoparticles that form during tempering (J. Millán, D. Ponge).

instable phases and the strain hardening effects that may result from local transformations, we observed that it is vital to design the phase stability and hence the strain hardening as a sequence of activated mechanisms that do not occur at the beginning of loading but gradually at later deformation stages, i.e. during ongoing loading at higher deformations.

Examples for successful new alloy design directions resulting from this strategy are maraging TRIP steels, TWIP- and TRIPLEX steels, Ti- and Fe-based GUM alloys, and ductile Mg.

A further essential detail pertaining to this strategy is the observation that the nanostructuring of such instable second phases leads in many cases to a profound increase in ductility without loss in strength. Examples are novel superplastic steels [88]; ultra-fine grained dual phase and C-Mn steels [55,58-63]; ultrastrong maraging-TRIP steels that are rendered ductile by the stabilization of retained austenite, formation of new instable re-austenitization layers on the former martensite lath grain boundaries, and intermetallic nano-precipitates, Figs. 13,14 [1,14]; nanotwin formation in Fe-Mn-C TWIP steels [15,21]; amorphous steels containing nanocrystalline second phases; weight-reduced Fe-Mn-Al-C steels containing nano-sized kappa carbides, Fig. 12

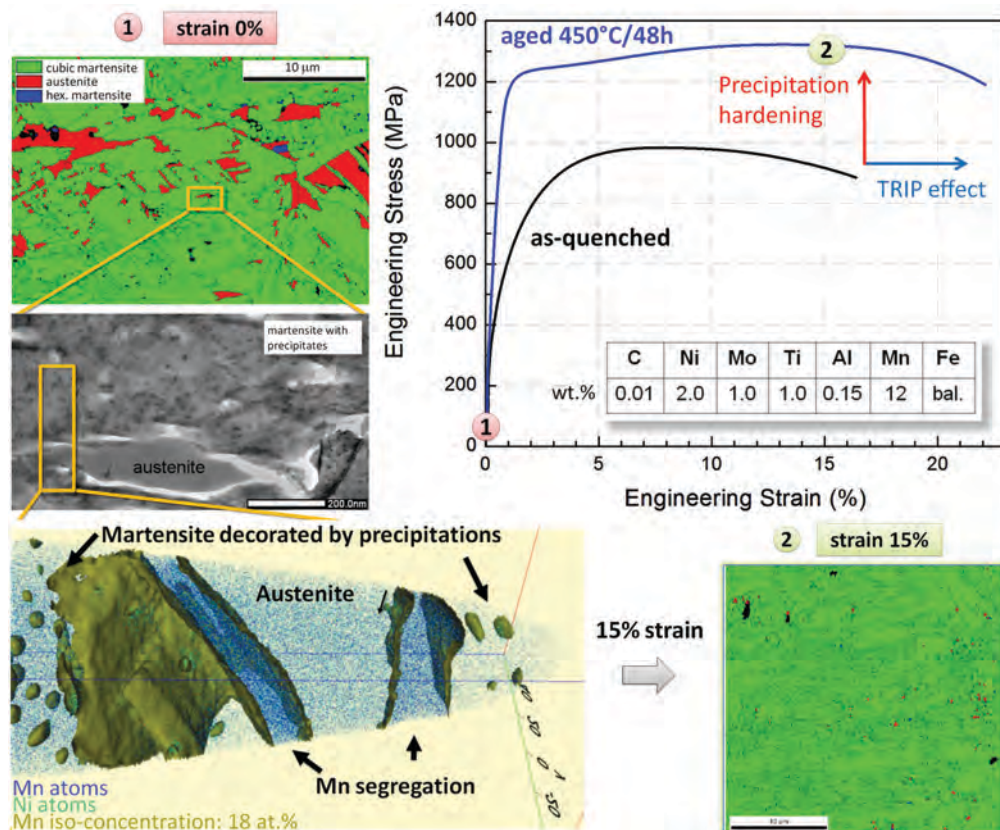


Fig. 14: The stress-strain curves illustrate the increase in strength from precipitation hardening and ductility enhancement from the TRIP effect. At 0% strain (1), the electron backscatter (EBSD) phase map shows significant amounts of retained austenite. Upon 15% straining (2), the retained austenite disappears in an EBSD phase map taken at the same magnification. The atom probe tomography analysis shows nanoparticles inside the martensite matrix and precipitate-free austenite regions. The Mn enriched layers (up to 27 at.%) at the interfaces between austenite and martensite is due to partitioning, subsequent austenite reversion, and kinetic freezing of Mn in the interface region [1,37,38].

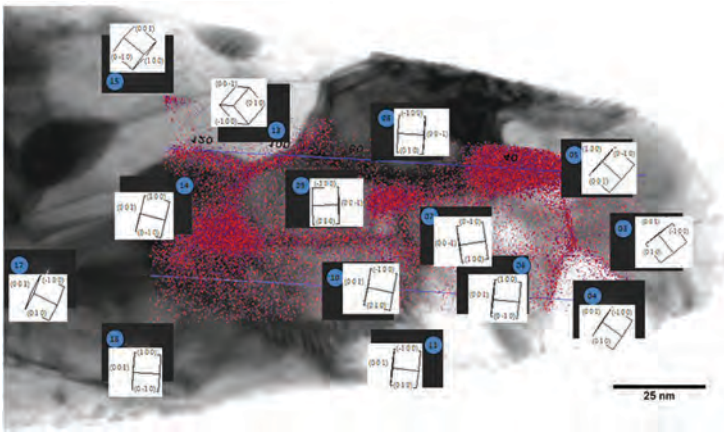


Fig. 15: Joint determination of the crystallographic orientation of the carbon-decorated subgrains (carbon atoms in red) and their chemical composition in pearlitic ferrite by TEM diffraction and APT (6.02 GPa UTS cold-drawn Pearlite -> annealed for 2 minutes at 400°C) (M. Herbig, Y.J. Li, P. Choi, S. Goto, D. Raabe, R. Kirchheim).

[39]; and nanostructured pearlite [41-43], Fig. 15. Regarding the latter material we currently hold the record of the world's strongest bulk structural alloy having a yield strength of about 6.3 GPa [43].

II. New insights: Advanced characterization of complex materials

The second field of long term developments is the development of a sequence of characterization methods that matches the hierarchy inherent in complex metallic micro- and nanostructures. This means that we require adequate structure and composition mapping at all scales that matter for understanding and quantifying the lattice defect populations that lead to the desired mechanical properties addressed above.

Mesoscopic characterization of the chemical and microstructural homogeneity of cast, formed, and heat treated samples can be conducted by using optical and scanning electron microscopy (SEM) in conjunction with EDX (energy dispersive x-ray spectrometry) and high resolution EBSD (electron back scatter diffraction). As suited SEM for this purpose we usually use a JEOL JSM-6500F field emission scanning electron microscope (FE-SEM) operated at 15 kV. The EBSD scans can be carried out in large areas or at high resolution down to a step size of 40 nm for the determination of phase patterning. When the 3D topology of the second phases is of high relevance 3D EBSD can also be used. This device consists of a dual beam set-up where we use fully automated serial sectioning and EBSD scanning cycles to reconstruct the microstructures in full 3D (see p. 117).

Strain-hardening phenomena in crystalline metallic act essentially through the reduction

of the dislocation mean free path, for instance, through smaller grain sizes (UFG), mechanical twins (TWIP), cell walls, or phase transformations (TRIP). All these additional interfaces act as obstacles to dislocation glide. Mechanical twins in TWIP steels are extremely thin, and hence are generally studied by transmission electron microscopy (TEM). However, TEM is limited when it comes to the quantitative characterization of highly heterogeneous microstructures, such as encountered in deformed TWIP steels. Another microscopy technique for characterizing deformed microstructures is electron channeling contrast imaging (ECCI). ECCI is a scanning electron microscopy (SEM) technique that makes use of the fact that the backscattered electron intensity is strongly dependent on the orientation of

the crystal lattice planes with respect to the incident electron beam due to the electron channeling mechanism [15,21,22]. Slight local distortions in the crystal lattice due to dislocations cause a modulation of the backscattered electron intensity, allowing the defect to be imaged. For quantitative characterization of dislocation structures (e.g. Burgers vector analysis) and to image these structures with optimal contrast, it is required to conduct ECCI under well-controlled diffraction conditions as dislocation imaging is obtained by orienting the crystal matrix exactly into Bragg condition for a selected set of diffracting lattice planes. To date the only method that was utilized for performing ECCI of dislocations under controlled diffraction conditions is based on electron channeling patterns (ECPs). The drawback of this technique is the requirement of a large final aperture to allow the beam to cover a large angular regime, leading to very low spatial resolution which is almost two orders of magnitude above the resolution of EBSD. This shortcoming reduces its application to the imaging of dislocation structures in lightly deformed metals. This also explains the limited number of works on the use of ECCI for imaging dislocation structures. In the past years we have developed a novel set-up for the ECCI technique under controlled diffraction conditions where the crystal orientation is obtained by means of EBSD. This set-up provides an efficient and fast means to perform ECCI of dislocations under controlled diffraction conditions with enhanced dislocation and interface contrast [15,21,22], Figs. 6,7,9.

When higher resolutions are required for nanostructure analysis, transmission electron microscopy (TEM) is applied. For TEM sample preparation the material is usually first thinned to a thickness below 100 μm by mechanical polishing. Standard 3-mm TEM discs are then punched and electropolished



into TEM thin foils using a Struers Tenupol twin-jet electropolishing device. The electrolyte typically consists of 5% perchloric acid (HClO₄) in 95% ethanol cooled to -30°C. Alternatively FIB thinning is possible too using our FEI nanolab dual beam system. The thinned specimens can then be investigated in the field emission transmission electron microscope JEOL JEM 2200 FS operated at 200 kV. The analysis are usually carried out in scanning TEM mode (STEM) using a bright field (BF) detector.

For yet higher resolution, specifically regarding the local chemical composition, nanostructure characterization via atom probe tomography (APT) is conducted. APT characterization is highly suited to better understand nanostructural changes in non-equilibrium alloys such as addressed by our group [1,9]. Its results can be compared to *ab initio* or conventional thermodynamic predictions regarding chemical phase composition or partitioning. APT characterization is carried out using a state-of-the-art local electrode atom probe. This instrument provides three-dimensional elemental maps in real space with a maximum field of view of 200 nm. Both, structural and spatially resolved chemical analyses can be realized with sub-nanometer resolution. Special features of the installed instrument are a wide-angle reflectron, which enables high mass resolution (and therefore the analysis of multi-component alloys and detection of low elemental concentrations) and an ultrafast laser, which allows for the analysis of non- and semi-conducting materials. By applying high-resolution electron microscopy as a complementary technique, we are capable of identifying not only the thermodynamic and compositional but also the structural information at near atomic resolution, Fig. 16.

III. New predictions: Multiscale models for quantitative simulations

For the alloy design strategy outlined above the prediction of accurate phase diagrams and of non-equilibrium phase transformations is a key element. While equilibrium data for stable phases are straightforward to measure and thus commonly available with high precision it is principally impossible to synthesize unstable bulk phases. Deducing their thermodynamic or mechanical properties is therefore only indirectly possible by e.g. epitaxially stabilizing such phases on suitable surface substrates (restricted to thin films only) or by extrapolating from the stable regime into the unstable one. In both cases the practical applicability is limited, often requires complex and expensive experimental setups, and provides large and often hard to estimate error bars. *Ab initio* calculations as a basis for searching unstable phases such as conducted on the department of J. Neugebauer is hence the basis and starting

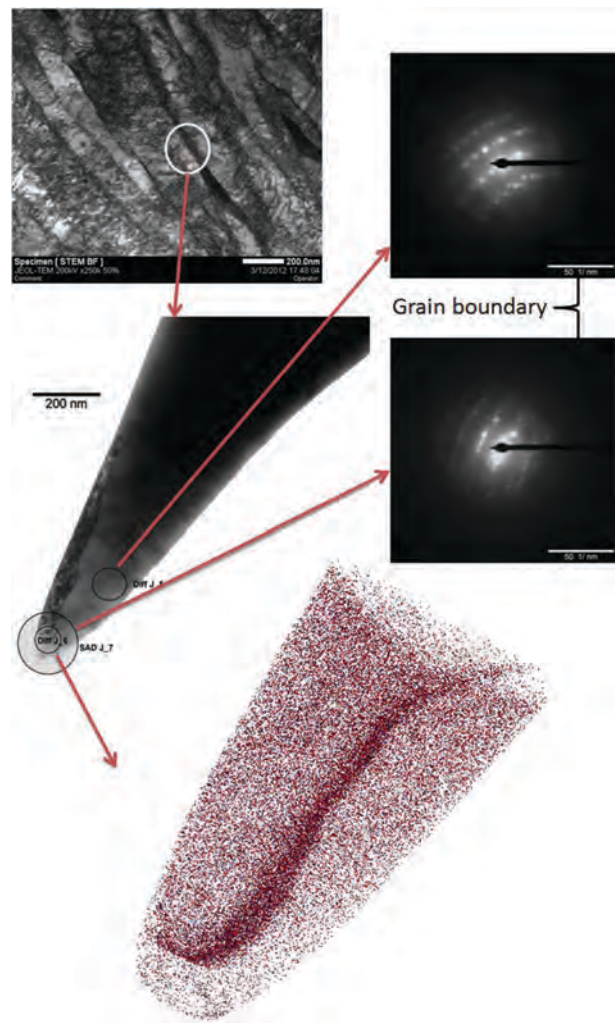


Fig. 16. Example of a site specific joint STEM-APT analysis of a grain boundary in a Fe-C-Mn martensite alloy. The dots indicate the positions of carbon atoms as measured by atom probe tomography. The joint analysis reveals strong segregation of carbon at the lath martensite grain boundary. The misorientation of this lath martensite interface amounts to about 7°. The depth of the evaporated volume is approximately 180 nm (M. Kuzmina, D. Ponge).

point for corresponding multiscale simulations of corresponding strain hardening phenomena that are based on non-equilibrium transformations (e.g. in TRIP, TWIP or GUM steels) [1,3].

To overcome the gap between the scale that is accessible to corresponding *ab initio* calculations predicting for instance phase stability, these data must enter into mechanism-based strain hardening models at the lattice defect scale. Examples are the use of *ab initio* calculated stacking fault energy values in a Fe-Mn steel that enter as an activation barrier into the cross slip term of a dislocation rate model or into the activation stress of a mechanical twinning event. Such multiscale approaches are often not restricted to bridging length scales but equally important to bridge time scales or sampling high dimensional configuration spaces.

Important examples from the past 6 years where such hierarchical scale-bridging concepts were realized in cooperation projects between our department and that of J. Neugebauer were the prediction of elastic constants of polycrystals by combining single crystal *ab initio* calculated elastic tensors with homogenization concepts developed in theoretical mechanics; the brittle-to-ductile transition behavior of Mg–Li alloys over the entire composition range;

the activation of mechanical twinning in TWIP steels as a function of chemical composition and stress levels (Fig. 6); the prediction of B2 and Heusler-type nano-particles in maraging steels, Figs. 13,14 (see p. 101), and Ti-based instable BCC and related Gum alloys which are characterized by large plastic yet hardening-free deformations (see p. 113). Further details about some of the developed multiscale concepts were part of the last bi-annual report.

Spirit and Outreach

Projects within our group and also among the departments are pursued in an interdisciplinary and team-oriented spirit. Scientists in our department come from such different backgrounds as metallurgy, physics, materials science, mechanical engineering, informatics, chemistry, and biology. Projects are conducted in an atmosphere of mutual inspiration, respect, communication, and cooperation. Paramount to the success of our work is the close exchange among theorists and experimentalists and an open minded attitude among the different disciplines.

The working atmosphere was during the past years dominated by an international flair bringing together young scientists and visiting scholars from Argentina, Australia, Bangladesh, Belgium, Brazil, Bulgaria, Colombia, China, Egypt, France, Germany, India, Indonesia, Iran, Japan, Jordan, Korea, Mexico,

Nigeria, Romania, Russia, Sweden, Spain, Ukraine, Poland, The Netherlands, Turkey, UK, Ukraine, USA, and Venezuela. Our international orientation is also reflected by our extramural cooperation partners, namely, Prof. Schneider, Prof. Bleck, Prof. Mayer, Prof. Friedrich, and Prof. Gottstein (RWTH Aachen, Germany), Prof. Dunin-Borkowski (Ernst Ruska-Centre, Research Centre Jülich, Germany), Prof. Rollett and Prof. Rohrer (Carnegie Mellon University, USA), Prof. Lebensohn (Los Alamos, USA), Prof. Radovitzky (MIT, USA), Prof. Mao (University of Science and Technology Beijing, China), Prof. Sandim (University of Lorena, Brazil), Prof. Bieler and Prof. Crimp (Michigan State University, USA), Prof. Mason (Albion College, USA), Prof. Hono and Prof. Adachi (National Institute for Materials Science, Japan), and Prof. Kobayashi (Tohoku University, Japan).

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Research Projects in Progress

Microstructure and Alloy Design (D. Raabe)

Khorashadizadeh, Raabe: Deformation-induced orientation laminates and orientation patterning in single- and polycrystals

Raabe, Gutierrez, Zaefferer: Fundamentals of soft magnetic Fe–Si transformer steels

Sandlöbes, A. Eisenlohr, Raabe: Microstructure and mechanical properties of Mg–Li alloys

Sandlöbes: Synthesis and Characterization of Fe-Mn reference materials

Sandlöbes: Constitutive modelling and microstructural validation for crystal plasticity finite element computation of cyclic plasticity in fatigue

Sandlöbes, Friak, Zaefferer, Raabe, Neugebauer: Fundamentals of the ductilization of Mg alloys microalloyed with rare earth elements

Theory and Simulation (F. Roters)

Eisenlohr, Roters: Development of a scale bridging method for describing deformation and intercrystalline fracture in Molybdenum

Eisenlohr, Roters, Bieler, Crimp, Raabe: Physically based approach for predicting and minimizing damage nucleation in metals

Raabe, Roters, Tasan, Diehl, Eisenlohr: Simulation of the mechanical response of stable dualphase steels

Roters, Eisenlohr: Materials World Network: Physically based approach for predicting an minimizing damage nucleation in metals

Steinmetz, Zaefferer, Raabe, Roters, Eisenlohr: Twinning mechanism in Mn TWIP steels

Diffraction and Microscopy (S. Zaefferer)

Davut, Elhami, Zaefferer: Relationship between microstructure and damage mechanisms in multiphase steels

Gutierrez, Zaefferer, Raabe: Local mechanical textures and properties of Mn-based steels

Jäpel, Zaefferer: Local strain determination in Mn-based steels

Khorashadizadeh, Raabe, Zaefferer: 5D Grain boundary characterization in ultrafine grained Cu–Zr alloys

Sandlöbes, Zaefferer: Fundamental investigation of the mechanisms of deformation and recrystallisation of cold deformable Mg alloys microalloyed with rare earth elements and microstructure optimization for the development of a new class of Mg alloys



Steinmetz, Zaefferer, Raabe: High resolution scanning electron back scatter diffraction experiments

Zaefferer: *In situ* SEM analysis and internal stress determination of threepoint bending tests

Zaefferer, Elhami: Characterization of the microstructure and deformation mechanisms in TWIP(XIP u. LIP) steels

Zaefferer, Raabe: Local textures and anisotropy in Mn-steels

Alloy Design and Thermomechanical Processing (D. Ponge)

Ponge, Raabe: OPTIBOS – New developments and optimization of high strength Boron treated steels through the application of advanced Boron monitoring techniques

Ponge, Springer, Raabe: Bladestrip - Innovative material production for blades and cutlery by strip cast technology

Raabe, Ponge, Millan, Springer: Mechanics of grain- and phase boundaries in multiphase steels

Biological Materials (H. Fabritius)

Fabritius, Wu: Biomimetic photonic crystals with mechanochromic properties based on cuticular scales of the weevil *Entimus imperialis*

Raabe, Fabritius: Generation of multifunctional inorganic materials by molecular bionics "Biogenic ACC Formation: The Mechanism of controlling Phase and Structure of Calcium Carbonate"

Raabe, Fabritius: Biomimetic Materials Research: Functionality by Hierarchical Structuring of Materials

Raabe, Fabritius: Crustacean skeletal elements: variations in the constructional morphology at different hierarchical levels

Atom Probe Tomography (P. Choi)

Choi: Thermal stability of metal nitride superlattices studied by means of Atom Probe Tomography

Choi, Cojocar-Mirédin, Raabe: Characterization of CIGS Solar Cells by Atom Probe Tomography

Choi, Tytko, Raabe, Povstugar: Thermal stability of metal nitride superlattices studied by means of atom probe tomography

Cojocar-Mirédin, Raabe: Optimization of solar cells efficiency based on 3-dimensional chemical analysis at atomic-scale

Jäggle, Choi, Raabe, Hickel, Neugebauer: Atomic scale investigation of the kinetics of nano-precipita-

tion in Fe–Si–Cu alloys using atom probe tomography and *ab initio* informed Monte Carlo methods

Li, Choi, Goto, Kirchheim, Raabe: Fundamentals of the strength of pearlite

Povstugar, Choi, Tytko, Raabe: Atom probe tomography of the chemical composition of interfaces in Ni-base superalloys

Raabe, Schneider, Choi: Topological Engineering of Ultra-Strong Glasses

Computational Mechanics of Polycrystals (P. Eisenlohr)

Eisenlohr, Roters: Development of a scale bridging method for describing deformation and intercrystalline fracture in Molybdenum

Eisenlohr, Roters, Bieler, Crimp, Raabe: Physically based approach for predicting and minimizing damage nucleation in metals

Roters, Eisenlohr: Materials World Network: Physically based approach for predicting and minimizing damage nucleation in metals

Zambaldi, Eisenlohr: Characterization and Modeling of the Interplay between grain boundaries and heterogeneous plasticity in titanium

Theory and Simulation of Complex Fluids (F. Varnik)

Varnik, Krüger, Raabe: Experimental and theoretical investigations of the dynamics of collective phenomena in blood I: Idealized vesicle/fluid droplet models

Varnik, Raabe: Nonequilibrium flow at gradient surfaces: multicomponent fluids

Combinatorial Metallurgy and Processing (H. Springer)

Ponge, Raabe, Springer, Belde, Yuan: Microstructure, austenite reversion and forming properties of martensitic Cr steels

Ponge, Springer, Raabe: Bladestrip - Innovative material production for blades and cutlery by strip cast technology

Adaptive Structural Materials (C. Tasan, B. Grabowski CM Dept.)

Tasan, Grabowski, Raabe, Neugebauer: SMART-MET - Adaptive nanostructures in next generation metallic materials: Converting mechanically unstable structures into smart engineering alloys



Department of Structure and Nano-/Micromechanics of Materials

G. Dehm

Introduction

Gerhard Dehm and three of his PhD students moved from the Erich Schmid Institute of Materials Science of the Austrian Academy of Sciences and the Department Materials Physics of the University Leoben to MPIE on 1st of October 2012. The newly formed department will be structured in 5 scientific groups working in the field of

- Nano-/Micromechanics of Materials,
- Advanced Microstructure Characterization,
- Nanotribology,
- Synthesis of Nanostructured Materials,
- Intermetallics.

All 5 groups will be interlinked to understand the mechanical response of materials focusing on small length scales by applying novel nano-/micromechanical approaches combined with advanced microstructure characterization techniques. The gained knowledge will be used to develop and improve nanostructured and intermetallic materials. Currently, most positions of the group leaders are vacant except for the already established scientific

group Intermetallics which is headed by Dr. Martin Palm and Dr. Frank Stein. For the research group Nano-/Micromechanics of Materials a group leader has been identified and will start with 1st of March 2013.

The newly formed department needs dedicated laboratories space especially for the installation of an advanced transmission electron microscopy (TEM) facility. This facility will open new horizons for *in situ* studies of dynamic material processes, atomic structure investigations and chemical analysis at ultra-high spatial resolution for structural and functional materials and expands the already existing conventional TEM laboratory. The advanced TEM facility will be located in hall 8 and 9 which must be adapted to host all TEMs of MPIE and the corresponding infrastructure for sample preparation and analysis by metallography methods, optical microscopy, scanning electron microscopy and focussed ion beam microscopy. The planning of the reconstruction work of hall 8 and 9 has already started and the remodeled laboratories are expected to be available in fall 2014.

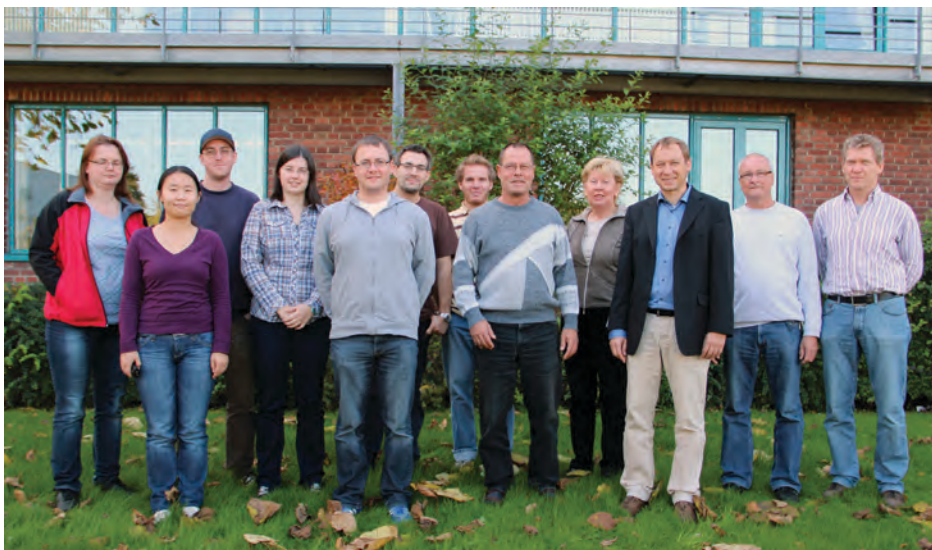


Fig. 1: First group picture of the newly formed department Structure and Nano-/Micromechanics of Materials taken at the beginning of October 2012.



Scientific Mission

Plasticity, fatigue, and fracture of materials are usually initiated by local deformation processes. Detecting and understanding the underlying mechanisms is the key to improve the mechanical performance and lifetime of **miniaturized materials** and also of **macroscopic materials**. Many **advanced structural materials** possess complex multiphase microstructures where the mechanical interplay of the different phases and their interfaces is poorly understood. Similarly, **functional materials** employed in modern micro- and nano-technologies are composed of material stacks and/or of different phases and possess confined geometries such as thin films, lines, rods, etc.. Such micro- or nano-sized materials often show a completely different mechanical performance compared to their bulk counterparts as a consequence of confinement effects. The **mission** of the Department Structure and Nano-/Micromechanics is

- to develop experimental methods to perform **quantitative nano-/micromechanical** and **tribological** tests for complex and miniaturized materials,
- to unravel the underlying deformation mechanisms by **advanced microstructure charac-**

terization techniques from the micrometer level down to atomic dimensions,

- to establish **material laws for local and global mechanical behavior**, and finally
- to generate **nanostructured materials** and high temperature **intermetallic materials** with superior mechanical properties.

The in-depth microstructure investigations include atomic resolved high-resolution TEM, analytical and conventional TEM, scanning electron microscopy with electron backscattered diffraction (SEM/EBSD), focussed ion beam microscopy (FIB), X-ray diffraction and synchrotron radiation techniques. A cornerstone will be the combination of advanced characterization and mechanical testing in form of *in situ* nano-/micromechanical experiments which will permit to simultaneously observe the microstructural changes while measuring the mechanical response. The gained insights will be used to quantitatively describe and predict the local and global material behavior and to design superior nanostructured materials and high temperature intermetallic materials by using local confinement effects. The synthesis of miniaturized nanostructured materials will be done by molecular beam epitaxy.

Scientific Concepts

The research work in the department **Structure and Nano-/Micromechanics of Materials** will focus on:

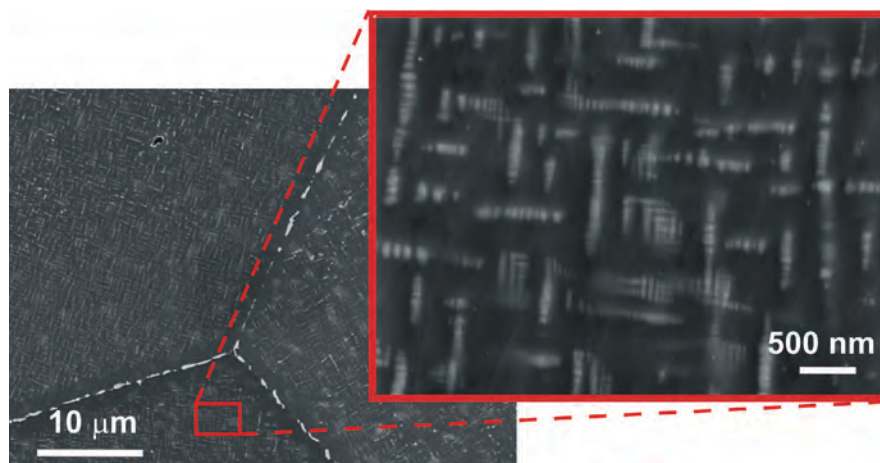
1. Development and application of novel nano-/micromechanical methods on bulk and miniaturized materials to study mechanical effects at small length scales.
2. Characterization of the microstructure and dynamic microstructural processes by advanced transmission electron microscopy methods, scanning electron and ion beam microscopy, and advanced X-ray techniques including synchrotron radiation.
3. Developing concepts to study nanotribology at metallic surfaces and to understand the processes of wear.
4. Synthesis of nanostructured materials and model systems by using molecular beam epitaxy.

5. Study of the structures, phase stabilities and phase transformations of intermetallic phases as a basis for the development of novel materials.

The research objectives in these five fields are summarized below.

1. In area 1 experimental approaches to study deformation phenomena at small length scales are developed and employed. The materials of interest are small scale materials as used in microelectronic and information technology as well as bulk structural and functional materials. Topics of interest are: onset of plasticity, length scale aspects of plasticity („size-effects“), brittle to ductile transitions especially in intermetallic materials, semiconductors, and ceramics, fracture behavior, crack growth and crack shielding phenomena, etc. The experiments will be conducted at different temperatures and under different environment (vacuum, N₂, etc.). Basic

Fig. 2: SEM and high-resolution SEM micrographs of a novel Fe_3Al -based alloy, strengthened by chains of coherent, nm-sized precipitates of Fe_2AlTa Heusler phase.



insights in the mechanical behavior of miniaturized materials and local material properties of bulk materials are the main task. This information may provide basic understanding of length-scale effects which in turn can be used for materials design concepts. Modelling of the mechanical phenomena will be done in close collaboration with the departments MA and CM, while environmental and chemical effects will be studied in collaboration with the department GO.

2. This area complements area 1 and provides the experimental methods to analyze the microstructure in advanced materials (Fig. 2) and their change during mechanical loading. One of the major methods will be *post mortem* and *in situ* TEM characterization to analyze the dominating deformation mechanisms related to micro-/nanomechanical materials response. In addition, the basic mechanisms in interface dominated materials and phase transformations will be studied. This includes transitions from interface sliding to interface fracture for heterophase boundaries exposed to deformation at different temperatures as well as size effects (confinement effects) in phase transformations of materials. Other possible questions involve ion exchange at interfaces, interface strain, and mechanical consequences. A technique which will be implemented as well in this area is X-ray diffraction (in-house laboratory and synchrotron radiation). Structures of interfaces determined by atomic resolved TEM investigations will be linked to atomistic calculations performed in the department CM. Similarly, chemical analysis by atom probe tomography and advanced EBSD techniques carried out in collaboration with the department MA will complement the research efforts of this area.

3. Materials are frequently in sliding contact with counterparts. This leads to friction and wear effects. While some basic concepts such as the Amontons-Coulomb Law and the stick-slip behavior are established, microstructural mechanisms which in turn lead to severe microstructural modifications in a surface zone are not yet fully understood. E.g. single crystal metals in sliding contact with a ceramic will develop a nanostructured zone with a very fine grain size. Understanding the underlying phenomena will open a link between tribology and microstructure for predicting materials behavior under sliding contact. Important parameters which will be studied include the influence of temperature and environment (liquid, dry, humidity, ...). Materials of interest stretch from structural materials, thin film systems, to selected biological materials. Cross-sections will be made using ion beam microscopy and studied using advanced microstructure characterization techniques including advanced TEM and X-ray diffraction methods. Close links to the department GO, MA, and CM are anticipated for the research area nanotribology to gain a basic understanding of chemical and structural changes in the surface-near zone.
4. Thin film deposition techniques are one way to produce nanostructured materials. Initially the focus will be laid on molecular beam epitaxy (MBE) of mainly metallic films and nanostructured metals. The systems which will be investigated include metal-polymer systems, well defined multilayers, nano-composite film structures, and growth of nanorods. Additionally, research in this area will include studies on metastable microstructures. Questions to be addressed are minimum grain size in nano-composites, evolution of nanostructures in non-equilibrium condi-

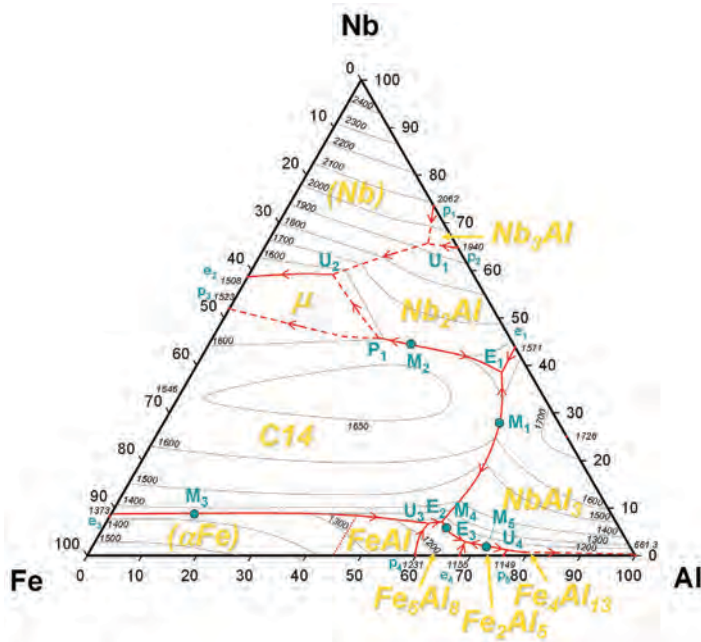


Fig. 3: Liquidus surface of the Fe–Al–Nb system as obtained from a combination of differential thermal analysis, scanning electron microscopy, electron probe microanalysis and X-ray diffraction.

tions exceeding solubility limits, and stabilization of metastable phases. This topic provides strong links to all three departments at the MPIE.

- Materials based on intermetallic phases comprise a new class of materials entering into application, e.g. TiAl compressor blades in the new GE_{NX}™ jet engines. The basis for any new material development is a sound understanding of the stability of the constituting phases in dependence of composition, temperature and time, i.e. knowledge of the respective phase diagrams. The structures, phase stabilities and phase transformations of intermetallic phases are therefore studied by microscopy, X-ray diffraction, electron probe microanalysis and differential

thermal analysis, among others. The results – often combined with CALPHAD modeling – are used to establish phase diagrams, isothermal sections and liquidus projections (Fig. 3). These are further employed for the development of novel materials. Current activities focus on Laves phases, Al-rich Ti–Al (c.f. p. 109) and Fe–Al intermetallic phases. All of the above topics, but specifically the basic mechanical properties of the intermetallic materials and their underlying phenomena, are studied in close connection with the other groups of the department. Further cooperation with all other departments exists, e.g. currently on rolling (MA), corrosion in steam (GO) and environmental embrittlement (CM) of Fe–Al based materials.



Max Planck Fellow Research Group on High Temperature Materials

A. Kostka, G. Eggeler

High temperature materials are an important material class for energy conversion and transportation. They represent a fascinating subject area for research in different fields of materials science and engineering. High temperature materials are usually difficult to process and manufacture. They generally have complex microstructures and, therefore, a good understanding of thermodynamic stability and microstructural evolution during high temperature exposure is required.

In the High Temperature Materials Group (HTM) we take a broad view on materials science and engineering of high temperature materials focusing on interesting physical, chemical, microstructural and mechanical topics. We presently work on (1) elementary dislocation processes during high

temperature and low stress creep of Ni-based single crystal superalloys, (2) the evolution of microstructure in 9-12% Cr tempered martensite ferritic steels (TMFS) during long term creep exposure, (3) the effects of grain boundary crystallography and chemistry on creep cavity nucleation and growth, and (4) the characterization of interfacial regions which form during joining of dissimilar materials due to multi atom interdiffusion processes. In the following we present three examples for the type of research performed in HTM.

The first example relates to our work in the field of Ni-based single crystal superalloys. Fig. 1 compiles scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs of important microstructural features that characterize these materials.

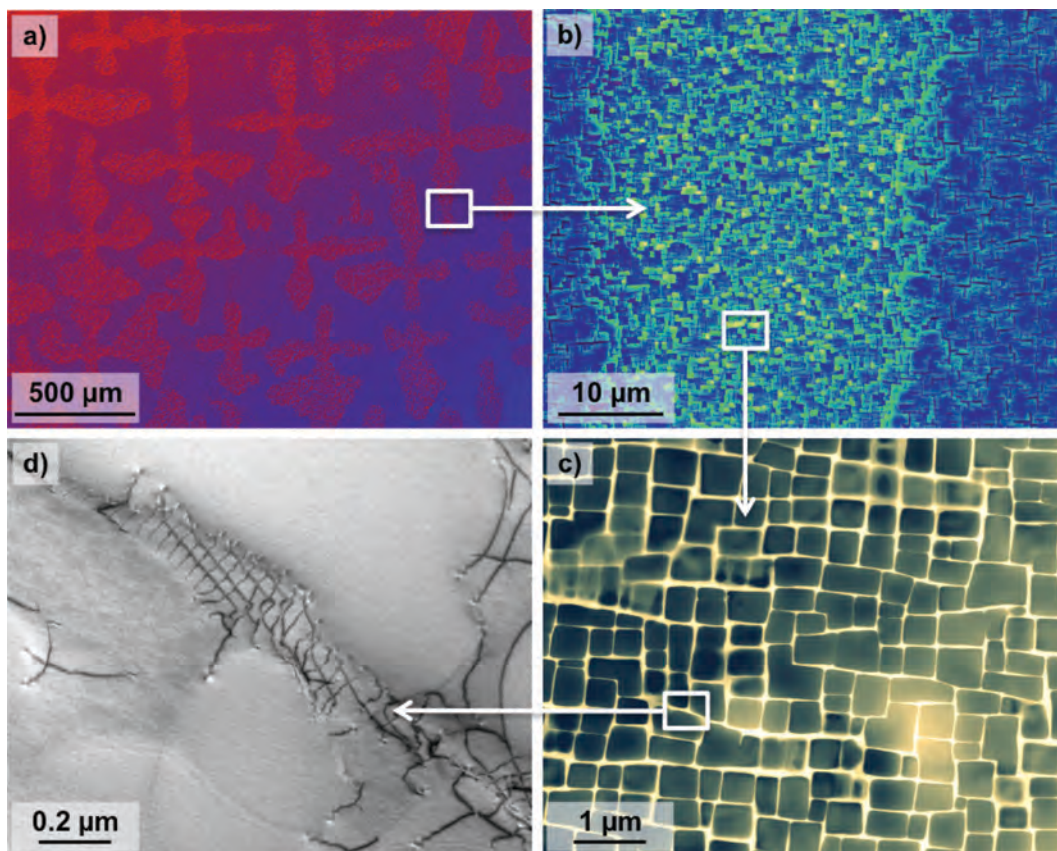


Fig. 1: Micrographs showing characteristic features of single crystal Ni-base superalloys. (a) SEM micrograph in the [001] cut revealing arrangement of dendrites. (b) SEM micrograph showing the transition between former dendritic and interdendritic regions. (c) TEM micrograph of γ/γ' -microstructure. (d) TEM micrograph showing dislocations in γ -channels of the γ/γ' -microstructure.



Fig. 2: Participants of the first SFB/Transregio 103 interaction week, Erlangen June 2012.

Performing research on single crystal superalloys with the types of microstructures shown in Fig. 1, HTM links MPIE research activities to the interdisciplinary research in the new collaborative research center SFB/TR 103, where single crystal super alloys are in the focus of interest. They represent key materials for turbine blades in modern gas turbines for aero engines and power plants. Worldwide air transportation and global energy production rely on this fascinating class of high temperature materials. Improvements in efficiency and emissions demand new concepts in single crystal technology, which require progress in four areas of expertise: (1) Basic understanding of all aspects associated with alloy composition / microstructure design and creep performance: microstructural instability during creep, elementary deformation and damage process during creep, dislocation reactions in single crystal Ni-based superalloys. (2) The continuous improvement and innovation of processing technologies for establishing specific nano- and microstructures with better homogeneity, improved creep and corrosion resistance (single crystalline solidification in a ionic liquid cooling bath, additive processing using selective electron beam melting, heat treatments under hydrostatic pressure, and coating technologies). (3) We pursue obtaining better knowledge of materials properties and microstructure through the use of improved testing procedures, either by mechanical measurements such as miniaturized creep and fatigue testing or by the use of latest high resolution characterization methods (high resolution, aberration corrected transmission electron microscopy, 3D atom probe). (4) Materials modeling bridging all

scales, from atomistic (*ab initio* methods, molecular dynamics) to mesoscopic (discrete dislocation modeling and thermodynamic / kinetic modeling of microstructural evolution) and macroscopic (physically sound constitutive equations). Modeling is to be applied to materials processing as well as high temperature behavior.

In addition to the SEM and TEM type of work as shown in Fig. 1, MPIE brings in expertise on the 3D atom probe method (Dr. P. Choi and Dr. I. Povstugar) that allows chemical analyse of $1 \mu\text{m}^3$ volumes to study elementary diffusion reactions in high temperature materials. In SFB/TR 103, HTM provides a detailed microstructural characterization of materials in the initial state and after well-defined creep periods. We explore the role of small and large-scale microstructural heterogeneities, provide quantitative data on porosity, dendritic structure and the evolution of the γ/γ' -microstructure. We focus on the elementary processes that govern the high temperature deformation of these materials. MPIE researchers participated in the first interaction week organized in Erlangen in May 2012 in the framework of SFB/TR 103, Fig. 2.

The second example of work performed within HTM considers the elementary processes (nucleation, growth kinetics, evolution) governing the formation of transition zones during high temperature joining of dissimilar materials. More specifically, the project focuses on the formation of intermetallic phases that form in the Fe-Al system during laser beam welding of iron to aluminium. The low density and good corrosion resistance of aluminum combined

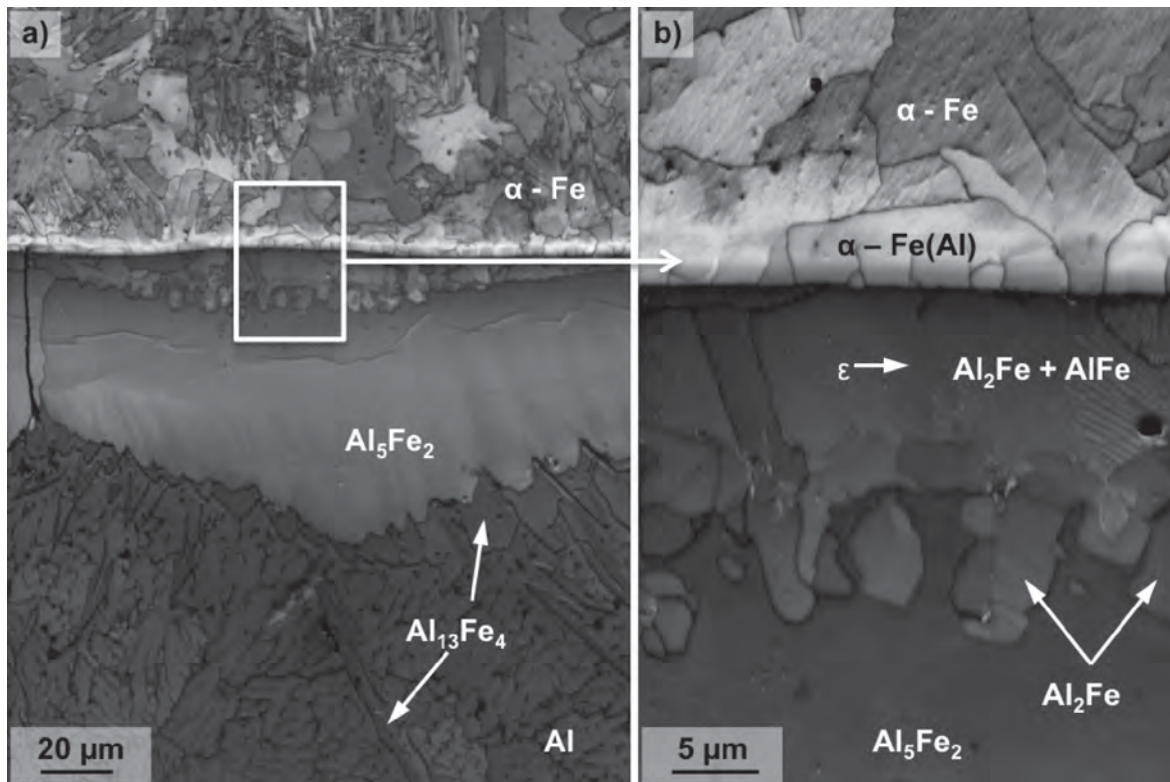


Fig. 3: EBSD quality maps from transition regions formed during laser welding of low carbon steel to aluminium. (a) Fast growth of the Al_5Fe_2 -phase in the direction perpendicular to the steel/aluminum interface. (b) Formation of new intermetallic phases between the steel and Al_5Fe_2 layer (DFG: KO 3998/1-1).

with the high strength and good formability of steel provides a highly versatile compound for engineering structural applications. Since Al-rich phases that typically appear in the Al-Fe system are extremely brittle, optimization of the joining process parameters which control the thickness of intermetallic layers are important. The main objective of HTM's work is to contribute to a better understanding of processes that govern the metallurgical reactions which occur when solid Fe/steel and liquid Al come in contact. Especially, the thermodynamic and kinetics of the formation and evolution of intermetallic compounds like Al_5Fe_2 and $Al_{13}Fe_4$ are in the focus of interest. During laser welding, only the Al is liquid while the steel plate remains solid. Rapid heating, cooling and associated temperature gradients at the solid steel plate/liquid Al interface dramatically affect the composition and morphology of the reaction compounds. Moreover, local temperature gradients result in the formation of new phases, as illustrated in Fig. 3.

As a third example, we present some results which were obtained in a project that focusses on the stability of phases in tempered martensite ferritic steels (TMFS) subjected to a long term creep

exposure. The project aims at understanding the nature of microstructural evolution resulting from long-term creep of TMFS at temperatures up to 600°C. The identification of the elementary processes that govern nucleation and growth of the Laves phase in TMFS is the main scientific objective of the project. Formation of the Laves phase in TMFS occurs after long-term creep and has so far not yet been clearly understood. Its appearance may well downgrade mechanical properties. Our goal in this project can only be achieved by combining analytical transmission electron microscopy with a detailed analysis of chemical composition by atom probe analysis.

In the research on tempered martensite ferritic steels, detailed investigations of the evolution of grain boundaries and precipitates such as $M_{23}C_6$, VN, and the Fe_2Mo Laves phase after different stages of creep also need to be performed by using scanning electron microscopy (OIM analysis) and transmission electron microscopy, where several techniques are applied for collecting micrographs (BF, DF, HAADF STEM, EFTEM), diffraction analysis (SAD, NBD) and chemical spectra (EDS). An example is presented in Fig. 4 (see next page).

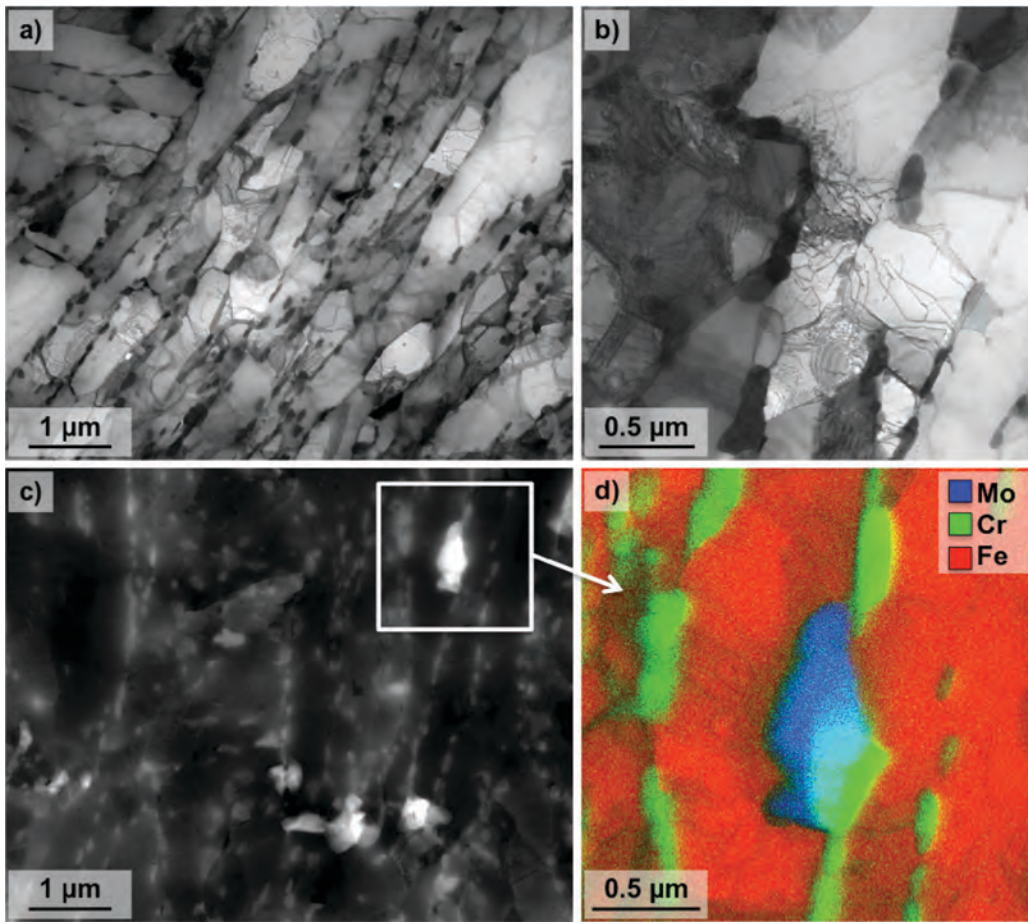


Fig. 4: TEM analysis of a 12%Cr TMFS after 51000 hours creep at 650°C, 120 MPa. (a) Bright field (BF) TEM micrograph showing $M_{23}C_6$ carbides decorating GB's. (b) Dislocations interacting with $M_{23}C_6$ carbides. (c) High-angle annular dark field (HAADF) micrograph reveals particles that differ by their composition. (d) Mo, Cr and Fe element maps overlay from the highlighted region in (c) showing $M_{23}C_6$ carbides and formation of Mo-rich Laves phase.

The three examples briefly introduced have in common, that non-equilibrium systems strive towards establishing an unknown thermodynamic equilibrium. Thermal activation allows for atomic mobility in the systems and plays a fundamental role in establishing microstructures and associated properties. The microstructure (constituent phases, particles, interfaces, defects) and related mechanical

features (external and internal stresses) are important parameters that affect the reaction path towards thermodynamic equilibrium. HTM aims at stimulating research related to the science and technology of high temperature materials. HTM also promotes activities that help to develop new materials and processes which overcome limitations which currently hamper advances in high temperature technology.