PART II.

THE DEPARTMENTS

(in alphabetical order)

Department of Computational Materials Design

J. Neugebauer

Scientific Objective and Department Structure

One of the major challenges to **simulate advanced materials** such as steels is their **structural, chemical and thermodynamic complexity** together with the fact that they are in realistic scenarios not isolated but in **an (often reactive) environment**. Most of the presently available simulation techniques address only a small part of this complexity and are restricted to a specific length scale. The objective of the department is the **development of computational tools and strategies that are capable to deal with realistic materials and processes**, the application of which allows a close link to the experimental activities in house and of collaborators worldwide.

Achieving this goal requires novel **scale bridging multi-scale approaches** that link fully parameter-free *ab initio* calculations with technologically relevant materials properties as well as strategies to push the predictive power and the computational efficiency of existing methods to their limit. These methodological developments and applications in the CM are performed in six groups headed by internationally highly visible scientists. The specific topics of the groups have been chosen such that their respective methods, expertise and investigated materials are complementary and can be linked in order to address material classes and questions that escape a single method. The availability of these methods opened a very productive route to study for example the complex phenomena that control the mechanical behaviour of ultra-high strength, TWIP (twinning induced plasticity), TRIP (transformation induced plasticity) or pearlitic steels (see p. 183).

It further provided a close link to interpret or guide experimental activities such as, e.g. electron microscopy (department of Structure and Nano-/Micromechanics of Materials (SN) and the independent research group Nanoanalytics and Interfaces (NG)), atom probe tomography (department of Microstructure Physics and Alloy Design (MA)) or Kelvin probe technique (department of Interface Chemistry and Surface Engineering (GO)) (see p. 149). In this way industrially relevant material science questions such as electrochemistry (see p. 161), tribology (see p. 179), grain boundary embrittlement (see p. 173) and hardening in Mg alloys (see p. 141) have been addressed in collaboration with the other departments.

Fig. 1: *The CM (summer 2015).*

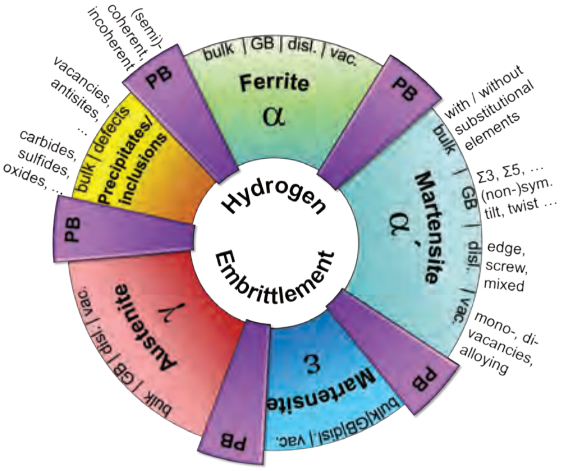


Fig. 2: *The spectrum of microstructure features that can interact with hydrogen and are therefore considered in the simulation of hydrogen embrittlement performed in the CM.*

The synergy between the groups within the CM is important to solve multi-scale problems such as hydrogen embrittlement (see p. 39), an effect that is strongly hampering the application of modern ultra-high-strength steels. Here, a complete picture of the detrimental effects of hydrogen (Fig. 2) could only be achieved by combining (i) the systematic and extensive *ab initio* study on its interaction with microstructure features such as vacancies, grain boundaries, precipitates in T. Hickel's group (Computational Phase Studies) with (ii) the atomistic description of plasticity related processes such as the hydrogen impact on dislocations and dislocation loops in B. Grabowski's group (Adaptive Materials) and (iii) the continuum investigations on the role of surface or interface strains on the solubility of hydrogen in R. Spatschek's group (Mesoscale Simulations). Linking these activities and results provided a unique insight into the various stages of hydrogen embrittlement and delayed fracture and allowed highly productive collaborations with experiments in house (MA, GO), with industry (e.g. projects funded by the European Commission such as HYDRAMICROS coordinated by T. Hickel), large scale research projects such as the DFG Collaborative Research Centre (see p. 52) or with other theory groups (see p. 53).

A key to successfully addressing this wide range of scientific questions was the strong methodological expertise that has been built up in the department over the last reporting periods. Only the availability of this expertise on advanced and highly accurate electronic structure calculations and their combination with thermodynamic, mechanical or chemical concepts enabled novel approaches and strategies that include contributions and mechanisms relevant in real materials, but that so far were impossible to compute with existing *ab initio* approaches [1]. One such example is a new formalism (see p. 177) for a fully *ab initio* description of magnon-phonon coupling, i.e., the effect magnetic excitations have on atomic vibrations and thermodynamic stability at higher temperatures [2]. By combining Spin-Quantum-Monte-Carlo methods with the spin-space-averaging (SSA) approach developed by the department in the previous reporting period, it became possible to understand this mechanism and to achieve an accuracy that agrees well with experiment. Since this effect is the major cause of the high temperature softening of ferritic steels, our insights can support the efforts in the MA to improve the mechanical properties of such steels. Other examples of novel methodological approaches that have been achieved based on the systematic developments of the last years are a highly efficient concept of computing anharmonic free energy contributions [3] that opens the route towards routinely including them in *ab initio* calculations or a generalization of the widely used Arrhenius concept to describe point defect concentrations [4]. The latter revealed that previously accepted and in compilations listed defect formation energies have to be revised by 10-20%. These methodological developments have been achieved by combining the expertise of T. Hickel's and B. Grabowski's group and have been published in top journals in the field (Phys. Rev. Lett., Phys. Rev. X).

Next to the long term development of *ab initio* based thermodynamic approaches, a major strategy in the last period was to use the broad materials expertise of the department, ranging from steel related systems over oxide/semiconductor topics to biomimetic materials, to link fields that so far were methodologically not connected. An example in this respect is the transfer of defect concepts that are well established in the semiconductor community to electrochemistry in the group "Electrochemistry and Corrosion Sciences" headed by M. Todorova. This "translation" made the concepts useful for both communities and allowed to use extensive sets of point defect calculations performed in semiconductor physics to understand corrosion of protective oxide layers. For example, this approach revealed that neutral oxygen vacancies rather than charged vacancies as always assumed in electrochemistry are relevant for the growth of the protective oxide layer [5]. Another example for a successful link of two different fields is the development of an analytical approach with atomistic resolution by G. Leyson (Humboldt Fellow) that connects mechanical and thermodynamic concepts and allowed to derive phase diagrams for defect-induced nanostructure phases [6]. Further, C. Freysoldt's and L. Lymperaki's groups combined statistical mechanics concepts and growth simulations [7, 8].

To keep the expert knowledge despite the rapid and desired fluctuations of key scientists in the department, we continued the development of a Python based workbench called "PyIron" that combines all aspects of setting up complex simulations, performing accurate convergence tests and error analysis, handling large amounts of computer runs with advanced databases and visualization. This toolset allows to "conserve" the methodological expertise of the various groups by generating automatized simulation protocols and by guaranteeing the targeted high numerical accuracy. A new generation of Bachelor, Master and PhD students in the department used PyIron to handle projects consisting of several $10^4 \ldots 10^5$ jobs that would have been hard to control and analyze with existing methods. Examples where the tool has been successfully used are the identification of chemical trends of interstitials in metals by using concepts of machine learning [9] or the calculation of TTT (Time-Temperature-Transformation) phase diagrams, which are crucial for the control of precipitates in steels and whose complete derivation with atomistic concepts has not been reported in the literature before [10].

The scientific results were also made available to the community by many publications in high-ranking journals. In the reporting period the H index of the department has increased by 66% (15 → 25). Here, our review papers, e.g., on first-principles calculations for point defects in solids [11] or lambda-transitions in materials [12], as well as our interdepartmental collaborations, e.g., on TWIP-steels [13] and Mg alloys [14] encountered the greatest interest in the field.

To further stir and disseminate these developments in the scientific community, the scientists in the department have been very active in organizing and co-organizing key conferences and symposia. One highlight was the now 5th ADIS (*Ab initio* Description of Iron and Steels) symposium which was organized by T. Hickel and attracted again the international top experts to Ringberg Castle. He also successfully co-organized the Unary Workshop (Fig. 3) that brought together the CALPHAD and the *ab initio* community [15]. The department further organized symposia at leading materials science and physics conferences (see p. 219). The CM also successfully run small and highly focused meetings in emerging fields that were very well received by the community: For example, S. Hadian and B. Grabowski organized a meeting on grain boundary migration in Günzburg and M. Todorova and C. Van de Walle (UCSB) a meeting on bridging electrochemistry with semiconductor defect chemistry in Santa Barbara. Members of the department are also actively involved in representing the community: J. Neugebauer has been elected head of the division Metals and Materials in the DPG and as representative (Fachkollegiat) in the Theoretical Chemistry Division of the German Research Foundation (DFG) and became editor of a newly established Journal of the Nature Group (Computational Materials). We are also closely connected to the neighbouring universities in Bochum, Aachen, Duisburg-Essen and Paderborn by large scale joint projects and activities such as the Interdisciplinary Center of Advanced Materials Simulations (ICAMS; see p. 53), the International Max Planck Research School SurMat (see p. 47 (with J. Neugebauer as speaker) or teaching duties (see p. 230).

The high scientific reputation that members of the department receive is reflected by the large number of invited and keynote talks at the major international conferences in the field. Members of the department also received prestigious prizes: B. Grabowski got an ERC starting grant, B. Lange the Otto-Hahn medal for an outstanding PhD thesis or G. Leyson and S. Hadian a Humboldt research fellowship. It is also reflected in changes in the group structure since

Fig. 3: *The Ringberg Unary Workshop 2013 was one of several workshops organized by the CM in the reporting period. It was devoted to fundamental concepts of computational thermodynamics.*

leading scientists got prestigious offers at institutions worldwide. M. Friák, who from the beginning of the department had headed the very successful group "*Ab initio* thermodynamics", is now the leader of a large experimental and theoretical group at the Academy of Sciences of the Czech Republic. R. Spatschek, has built up over the last five years a highly productive group on Mesoscale Simulations that linked many of the atomistic concepts of the department to experimental activities. He accepted an offer on a joint professorship position at the Research Center in Jülich and the RWTH Aachen, which he started October 1st, 2015. The scientific expertise is kept up by maintaining strong links with these and other leaving scientists via joint projects and publications. Furthermore, a new research group "Electrochemistry and Corrosion" has been created and is headed by M. Todorova starting October 1st, 2015 (see p. 28). This group will provide a strong link to the activities in the GO, particularly to the groups of S. Wippermann, M. Valtiner and A. Erbe, but is also connected to the semiconductor/oxide activities in C. Freysoldt's group as well as to the thermodynamic sampling concepts in T. Hickel's and B. Grabowski's groups. L. Lymperakis became a project leader in a large EU project and heads the project group "Growth Modeling" that addresses a wide range of semiconductor related activities. In the following the group activities are briefly summarized:

Research Groups

Computational Phase Studies (T. Hickel)

This group is devoted to the physics of (meta) stable thermodynamic phases in metals as well as transitions between them. Its major vision is an *ab initio* based prediction of thermodynamic properties and bulk phase diagrams, being directly related to many technologically relevant mechanisms in metals. According to the spirit of the whole department outlined above, the group made in the reporting period substantial progress developing methods for an application to advanced material systems such as:

- The improvement of *ab initio* based methods to calculate anharmonic contributions to the free energy of metals caused by the interaction of phonons and of lattice and magnetic degrees of freedom. [2, 3]
- The comparison of *ab initio* determined thermodynamic properties with experiments and their combination with thermodynamic databases. [4, 16]
- The description and prediction of temperature and stress induced phase transitions and/or structural changes in shape memory alloys, steels and related materials. [17, 18]
- The energetics and kinetics of alloying elements, impurities and defects, and their relevance for embrittlement phenomena, precipitation and ductility of materials. [19, 20]

All these activities are characterized by **strong collaborations** with other groups in the CM, with other departments of the MPIE, as well as with academic and industrial partners in various research institutions. The Ringberg Unary workshop 2013, which was organized by T. Hickel, U.R. Kattner (NIST, USA) and S.G. Fries (ICAMS, Bochum), is a consequence of the world-wide interaction in computational thermodynamics (Fig. 3). It addressed the most promising concepts to improve the accuracy and physical fundament of thermodynamic databases regarding crystalline phases, liquid phases, lambda transitions in materials, effects of pressure and stress, and point defect thermodynamics [15]. As outlined in five large review articles (e.g., [12,21]), which came out of this workshop, the recent progress in combining *ab initio* calculations with thermodynamic concepts pushed the insights and achievements substantially forward for each of these topics. The group has continuously contributed to this development.

Anharmonic lattice vibrations, for example, form a particular challenge for the description of the crystalline state of materials at finite temperatures. We revealed that the asymmetric nature of the local potential for the nearest-neighbour atomic interaction provides the underlying physics for these excitations (A. Glensk, see also p. 171). Based on this insight, a highly efficient approach was developed and benchmarked for an extensive set of unary fcc metals [3]. Astonishingly, this study revealed that anharmonic heat capacity contributions can be of the same order as the quasiharmonic corrections due to thermal expansion.

Consequently, anharmonic lattice vibrations have also been taken into account for the Gibbs **energy of vacancy formation** in Al and Cu (A. Glensk). The resulting highly nonlinear temperature dependence in the Gibbs formation energy naturally explains experiments and shows that nonlinear thermal corrections are crucial to extrapolate high-temperature experimental data to T = 0 K [4, 11, 21]. The findings are related to the observation that the formation entropy of vacancies is not constant as often assumed, but increases almost linearly with temperature.

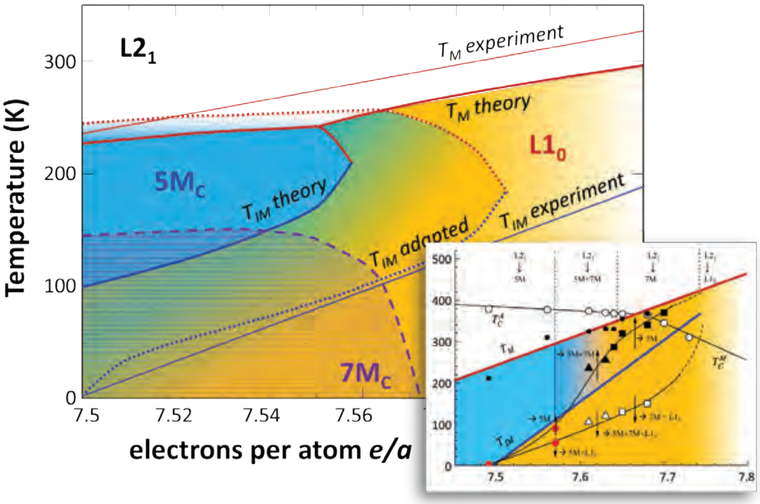


Fig. 4: *Ab initio calculated phase diagram of Ni$_2$Mn$_{1+y}$Ga$_{1-y}$. The martensitic transformation T_M (thick red line) separates the austenite from different martensitic phases. The theory predicts an intermartensitic transformation T_{IM} (thick blue line) between the 5M phase (blue-coloured area) and the L1$_0$ phase (orange). For comparison the experimental results are shown by thin lines and in the inset. The stability region of the commensurate 7M is indicated by a purple dashed line. Figure adapted from [25].*

The treatment of **magnetic excitations** within the scope of phase studies is another field of central interest, since its complexity and numerical challenge requires non-trivial solutions. We have developed a set of analytical and numerical methods, how in particular the quantum-mechanical character of this free energy contribution can be taken into account [22] and have applied them to magnetic elements, including Cr [16]. It is typically assumed for the computation of phase stabilities that an adiabatic decoupling of entropy contributions is present [12]. In the last years we realized, however, the importance of a magnetically driven modification of lattice vibrations not only in the paramagnetic limit, but already close to the ferro- to paramagnetic transition (F. Körmann, see also p. 177). Our developed temperature-dependent spin-space averaging (SSA) technique has led to phonon spectra that are in perfect agreement with recent sophisticated experimental findings [2]. Related approaches have also been developed to describe the magnetic influence on structural parameters such as stacking fault energies (I. Bleskov) [23]. In an alternative approach based on the itinerant coherent potential approximation, we additionally checked the impact of magnetic fluctuations on these results and found them to be small [24].

The investigations on **Heusler alloys** underline the need for accurately determined free energies. In the reporting period the presence of intermartensitic transformations in Ni-Mn-Ga alloys was a key question, due to the major importance for shape memory and magnetocaloric effects that make the material class interesting for applications (B. Dutta). Here, tiny energy differences between structures that only differ in small modulations are present. The successful clarification of experimental uncertainties not only about the chemical trend, but also about the physical origin of such transformations, is therefore a highlight of the present research activities (Fig. 4) [25]. The investigations of martensitic phase transformations have meanwhile even been extended to quaternary Heusler systems [17]. In collaborations with experimental partners within the DFG priority programme SPP1599, also other interesting phenomena of this material class have been explained by *ab initio* investigations [26, 27]. A rather surprising outcome was the identification of Heusler phases as precipitates in steels [28].

The free energy of formation of certain phases has besides cementite in steels (F. Körmann) [29] been further investigated for various **structural materials with high-potential for applications**, including the Q phase in Al alloys for light-weight constructions (A. Zendegani) [30], Laves-phases in Fe-Nb alloys for high-temperature energy applications (A. Zendegani), and various phases in Nd-Fe-B and Ce-Fe-Ti for hard-magnetic materials (H. Sözen).

In these studies we realized that a pure thermodynamic argumentation is often not sufficient to explain the experimentally observed formation of secondary phases. In particular in steel microstructures the **interfaces to the matrix material** can be of key importance for the precipitate structure and chemical composition. In the case of κ carbides (see p. 149), for example, we revealed that the elastic energy due to misfit strain explains a substantial deficiency of carbon in the precipitate phase (P. Dey) [31]. The situation is even more complicated in the case of cementite, when it forms at the interface between austenite and ferrite in a coupling process (X. Zhang). This is because three phases and a combination of the martensitic rearrangement of Fe atoms and a diffusion-driven separation of C atoms are simultaneously present. We have shown that a metastable intermediate structure (MIS) in the spirit of complexions can serve as a natural link between these phases and can explain the atomic process during decomposition (Fig. 5) [18].

Treating the interplay of nanodiffusion and structural properties was also decisive for the simulation of **mechanical properties** in high-Mn steels (I. Bleskov). The stacking fault-carbon interaction in these steels is characterized by an anti-Suzuki effect, i.e. the interstitial C atoms will diffuse away from the planar defect. Since the relevance of this process depends on the temperature imposed by the experimental conditions, we were able to explain different chemical trends observed in experiment [20]. These insights into atomic mechanism are decisive for an *ab initio* based prediction of deformation behaviour, e.g. the crash performance of modern steels [32] and have contributed to the success of the collaborative research centre SFB 761 “Stahl – *ab initio*” and its extension by another funding period starting in 2015.

A kinetic investigation of the precipitate formation has been performed for Al-Sc using **kinetic Monte-Carlo simulations** (A. Gupta) within the DFG priority programme SPP1713. The highlight of this work was the prediction of general features in the resulting time-temperature-transformation (TTT) diagrams, including the relation between the nose temperature for the fastest precipitate formation and the asymptotic temperature for the entropically-driven dissolution of all atoms in the matrix [10]. The fast determination of such trends would not have been possible without our Python based **workbench Pylron** discussed above. It is currently also used to identify fundamental rules for the solution of interstitial elements by analysing the results of high-throughput investigations (U. Aydin) and for running automated calculations with a prescribed error convergence (J. Jansen), which we consider as future challenge in the framework of integrated computational materials engineering (ICME).

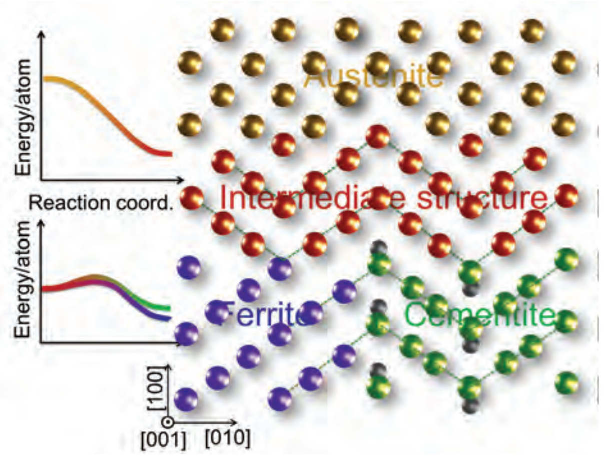


Fig. 5: *Representation of the atomistic mechanism of austenite decomposition including the effect of interfaces. Large spheres refer to Fe atoms in austenite (gold), the metastable intermediate structure, MIS (red), ferrite (blue) and cementite (green). Small dark spheres refer to C atoms. Dashed lines visualize the formed nano-twins during decomposition. The energy paths between the phases have been obtained by nudged elastic band calculations. Figure adapted from Ref. [18]*

The role of hydrogen for the stability of structural materials remained to be another important topic of the group that was triggered by various projects, primarily with industrial partners (see p. 39, see p. 163). In the last reporting period the investigations were focussed on a possible H enhanced decohesion of the interface between precipitates such as κ carbides (P. Dey), TiC (R. Nazarov) [33], and cementite (E. McEniry) [34] and the Fe matrix in steels. Further activities cover the interaction of H with vacancies (R. Nazarov) [19], chemical trends for the H solubility [35] and the understanding of the thermal desorption spectroscopy (E. McEniry).

Adaptive Structural Materials (B. Grabowski)

The general aim of the group is the design of advanced, next-generation structural materials based on innovative concepts driven by state-of-the-art simulation tools. To achieve this goal, also this group is focusing on further advancing the methods developed in the CM over the past years. These methods are rooted in accurate *ab initio* approaches and they extend to large scale molecular dynamics (MD) simulations based on empirical potentials and also to analytical approaches based on continuum theory. The group has a strong collaborative network within the MPIE (e.g., experimental ASM group in the MA) and with external partners from academia (e.g. Imperial College London or KTH Stockholm) and industry (Sandvik, Sweden). The projects investigated in the ASM group are ranging from simpler material systems, where the accuracy of the developed methods can be validated against experiment, to complex multiscale problems, where the focus is on understanding the atomistic mechanisms responsible for the experimental observations.

A core effort of the group is the development of efficient *ab initio* methods for highly accurate free energy determination at finite temperatures. This work is done in close collaboration with T. Hickel’s group. A thermodynamic software package is being jointly developed that already allows to routinely employ previously developed methods such as the *up-sampled thermodynamic integration using Langevin dynamics* (UP-TILD) method. We presently focus on computing phase stabilities of arbitrary structures, i.e. dynamically unstable solids, multicomponent systems, and liquids.

An important step in this direction has been recently taken with the introduction of the *two-stage up-sampled thermodynamic integration using Langevin dynamics* (TU-TILD) method [36]. This development is based on a collaboration with A. Duff (former member of CM) and M. Finnis (Imperial College London), who are experts in the field of interatomic potentials. Combining their knowledge with our expertise in describing vibrational free energies, the TU-TILD method was invented providing a large reduction in computational time (Fig. 6). The key idea is the introduction of an intermediate step based on optimized interatomic potentials. These potentials are fitted to *ab initio* MD trajectories at a specific volume and temperature. With this fitting procedure the transferability of the potentials is lost — a requirement in the usual construction of empirical potentials — but transferability is not needed for the TU-TILD method, since the potentials are only used as an optimized reference for thermodynamic integration. With this method we have enabled not only highly accurate and efficient calculations of the full vibrational spectrum, but also a very versatile approach allowing us to treat arbitrary structures.

Several projects within the ASM group are presently focused on exploiting the full power of the developed thermodynamic approaches: One of them is devoted to a highly accurate description of the temperature dependent phase stabilities in Ti (D. Korbmacher). This is a non-trivial task because the high temperature bcc phase is dynamically unstable and thus previously established rules fail to apply. A particularly important point is to understand the finite size constraints on the bcc to hexagonal (ω) phase transition, which we study with TU-TILD potentials. In another project, we further transfer and extend the knowledge gained for pure Ti to the binary Ni-Ti system (S. Maisel), which is technologically important its shape memory effect. The challenge in this project is to couple the vibrational excitations responsible for the stabilization of the dynamically unstable phases with the configurational entropy, which we tackle by integrating the cluster expansion method into our previous developments. Another exciting thermodynamic for development in the ASM group is the calculation of *ab initio* free energies of liquids (L. Zhu). The difficulty in determining the thermodynamics of liquids is that, in contrast to solid phases, no fixed lattice is available which could be used as a starting point. Our solution to this problem employs several intermediate thermodynamic integration steps between solid and liquid including also TU-TILD potentials.

Several collaborative projects broaden our spectrum of thermodynamic activities. A recently started project on temperature dependent stacking-fault-energies establishes a collaboration with R. Sahara (NIMS, Japan) who received a grant to stay for one year in our group. In another project we investigate the impact of lattice vibrations on local magnetic moments together with B. Alling (Linköping University, Sweden), who is presently a guest researcher under the Swedish International Career Grant. In a collaboration with A. Ready (Imperial College London) we apply our knowledge on bulk Ti and extend it to the description of defects (vacancies, impurity atoms, and their interactions), in order to understand the industrially relevant problem of low temperature creep in Ti alloys. Another problem of industrial relevance is tackled in collaboration with B. Kaplan and A. Blomqvist (Sandvik, Sweden). The goal is to establish an accurate thermodynamic database for Cr carbides which are a critical component in tool steels.

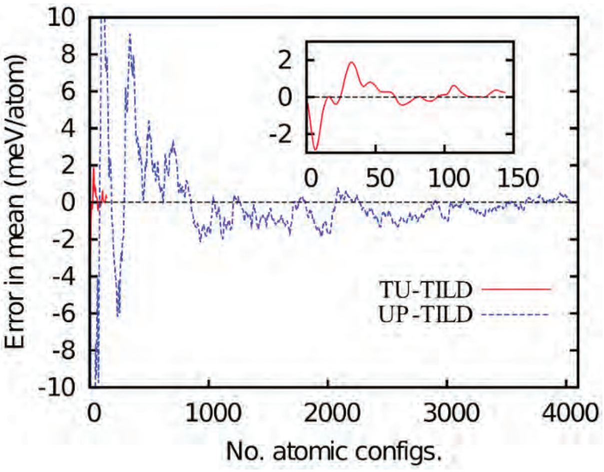


Fig. 6: *Example of the performance increase in computing ab initio free energies for ZrC by the newly developed TU-TILD method. Good statistical convergence can be now reached within a few hundreds of atomic configurations (red solid curve, inset) whereas several thousands of configurations were needed previously (blue dashed curve). Figure taken from Ref. [36].*

The projects described so far are based on standard approximations to the exchange-correlation functional within density-functional theory (DFT). For a wide range of materials these approximations provide an excellent description of finite temperature properties up to the melting point. However, for some materials such as Au severe discrepancies are found in comparison to experiment. In collaboration with S. Wippermann from the GO, we have recently extended the UP-TILD method allowing now to compute finite temperature properties, in particular anharmonicity, at a level beyond the standard approximations [37]. Applying the new method to Au we could show that the severe discrepancies introduced by the standard functionals disappear (see p. 171).

In addition to the efforts relating to thermodynamic properties, projects are carried out where we apply and extend our finite temperature expertise to kinetic processes. One example is the investigation of grain boundary migration using large scale MD simulations (S. Hadian), which is essential to predict microstructure evolution and thereby the mechanical properties of materials. The present knowledge of grain boundary migration is limited and discrepancies between theory and experiment exist. We could recently show, by overcoming the limits of state-of-the-art simulations and extending the simulations to fully 3D supercells and grain boundaries deviated from the symmetric case, new and unforeseen atomistic mechanisms occur, the implications of which are presently investigated. This work on grain boundary migration is well embedded into the strategic plan of the MPIE (see p. 40) and cover figure of this report) and also well received by the experts in the community as became evident on the grain-boundary-migration conference we have recently organized (http://gb2015.mpie.de).

An important backbone of the ASM group is the close collaboration with the experimental ASM counterpart in the MA headed by C. Tasan. The joint efforts of the theoretical and experimental ASM groups are guided by the general strategy established in the SMARTMET ERC project (see p. 50), with the main idea of developing smart metallic materials. Specifically, we investigate mechanisms responsible for the unique properties of high entropy alloys (see p. 147) and we also intensively focus on phase transitions in Ti alloys. Recently, we started to apply our knowledge on Ti alloys to investigate routes for designing self-healing metals. This effort is embedded into the DFG priority programme SPP1568, which intends to advance self-healing in all material classes. In our project, we study whether shape-memory-alloy nano-particles can be applied as self-healing agents [38]. In particular, on the theory side, we are performing large scale MD simulations of the interaction of a nano-particle with a crack (W.-S. Ko). Our results are important guidelines for the corresponding experimental efforts of the self-healing project.

Beyond the projects mentioned so far, which are mainly focused on analysing a specific length scale by a suitable method, we investigate also complex material problems that require the application of multiscale approaches. As part of the department-wide research on hydrogen embrittlement, we have, for example, recently developed an atomistically informed analytic continuum approach allowing to predict nano-hydride formation in the strain field of dislocations (G. Leyson) [6]. This approach is accurate and efficient and allows therefore to compute complete phase diagrams (Fig. 7) which can be passed on to higher level approaches like discrete dislocation dynamics or finite element analysis. This is an important step towards quantifying the effect of hydrogen localization around dislocations to fracture mechanisms. In another multiscale project, the mechanisms causing C supersaturation of the ferrite phase in a severely drawn pearlitic wire are investigated (A. Nematollahi). Such wires are the world record holders having the highest tensile strengths in structural materials with up to 7 GPa. The mechanisms causing these special properties are not yet fully understood, but atom probe tomography performed in the MA suggests that cementite decomposition and the resulting C supersaturation of ferrite is a decisive factor. A. Nematollahi has recently successfully finished his PhD thesis on this topic, where he employed different methods on various length scales showing that dislocations are the main source of the supersaturation. In addition to the thermodynamic stabilization of C around dislocations, he could show by atomistic barrier calculations and by solving a corresponding diffusion equation that there is a realistic drag mechanism which could lead to the observed cementite decomposition. These theoretical results nicely support and explain the complementary experimental observations performed in the MA and SN (see p. 183).

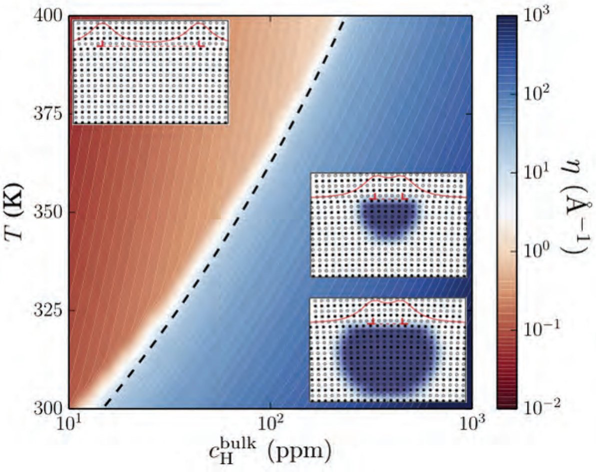


Fig. 7: *Example of a nano hydride phase diagram around an edge dislocation in fcc Ni as a function of bulk hydrogen concentration* c_H^{bulk} *and temperature T. The colour indicates the excess hydrogen, η,, per unit length of the dislocation. In the blue part of the phase diagram a nano-hydride is formed, whereas it is destroyed by configurational entropy in the red part. The three insets show a region around the dislocation core (indicated by the red lines) without and with nano-hydride (highlighted by the blue colour).*

Mesoscale Simulations (R. Spatschek; until October 1, 2015)

The research in this group is devoted to the understanding of **scale bridging phenomena appearing on dimensions between the atomic and continuum scales**. Various computational and analytical techniques, which are particularly tailored to the different applications, are used in this group. The further development and improvement of models and simulation techniques is also an important activity. In the following, recent key activities are briefly discussed.

The understanding of **hydrogen embrittlement** is a central topic for the group and linked to the SFB 761 (see p. 52). Together with T. Hickel's group, the site preference of hydrogen atoms in Fe-Mn alloys has been investigated. It turns out that H prefers a Mn-rich environment, which to a large extend can be attributed to volumetric effects [35]. Such ab initio information is further passed to continuum descriptions of coherent hydride formation in the bulk and near surfaces. We found that the hydrogen solubility limit near free surfaces is significantly lower due to elastic relaxation, which enhances the nucleation of detrimental brittle hydrides in these regions and at cracks (G. Gobbi, C. Hüter).

Within the DFG priority programme SPP1713 we investigate **bainite formation in partial press hardening processes** as a joint project between the MPIE Düsseldorf, RWTH Aachen University and IWT Bremen. Press hardening, also known as hot stamping, has become an important processing technology for the production of high strength steels mainly for automotive industry. Conventionally, the underlying concept is the rapid quenching of the austenite to the martensite state. Recent developments use interrupted cooling plus quasi isothermal holding in the bainite region, yielding partly bainitic structures with very attractive properties. This technique is called bainitic press hardening and it offers advanced strength-failure-strain combinations. We pursue a scale bridging description of the phase transformation kinetics during the forming process, which starts from fundamental microscopic properties and goes up to effective descriptions on macroscopic scales [39] (C. Hüter).

The thermodynamics and kinetics of **grain boundaries** has been investigated by means of amplitude equations approaches, which supplement conventional phase field models by preserving atomic resolution. The appearance of temperature dependent dislocation pairing transitions in symmetric tilt grain boundaries is found to be in agreement with predictions from atomistic simulations and phase field crystal simulations [40]. Shear coupled motion of grain boundaries is found to obey the geometrical model of Cahn and Taylor, including also grain rotation [41]. The methodology has also been applied to extended defects in nanowires, including scaling predictions for the growth conditions of coherent nanowires [42, 43] (C. Hüter, G. Boussinot, C.-D. Nguyen).

As a continuation of our activities on **grain boundary melting** we transferred our findings on short ranged interactions between adjacent grains to larger scales [44, 45]. These short range forces locally modify the thermodynamics on the nanometre scale and can induce grain boundary premelting of high angle grain boundaries below the bulk melting point. To understand the implications of these effects for the kinetics of melting processes along grain boundaries, we combined them with mesoscale concepts for microstructure evolution modelling. It turns out that the microscopic effects indeed can have a significant influence on the steady state velocity of the mesoscopic front propagation (Fig. 8) [46]. Whereas the used sharp interface approaches are particularly useful for a closed analytical understanding of the dependence on material parameters, actual simulations of grain boundary melting in polycrystalline materials are easier to perform using phase field methods. For that, we have investigated how the short ranged interactions are related to the intrinsic phase field model parameters for a quantitative mapping between the different methods [47]. A comparison between the predicted melting velocities from the sharp interface and phase field methods provides the tools for large scale simulations [48] (P. Bhogireddy, F. Twiste, C. Hüter).

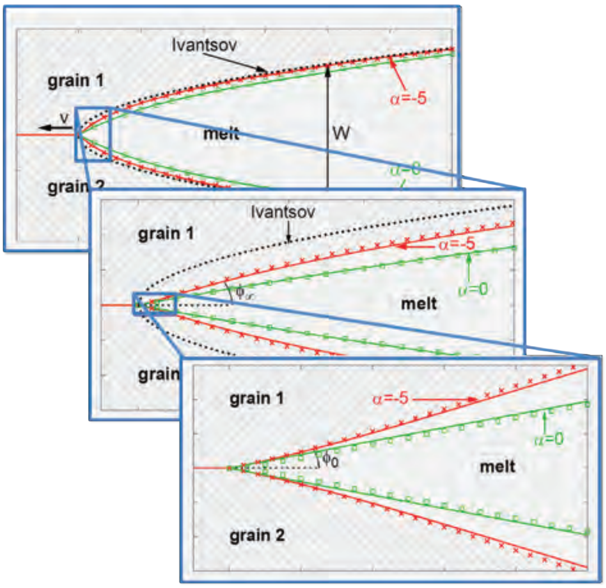


Fig. 8: *Hierarchy of scales for the melting along overheated grain boundaries. On the mesoscale (background) the melt front has a parabolic front. At the tip (magnified), a finite mesoscopic dihedral angle forms. On the nanometre scale (front panel) the solid-melt interfaces are not straight due to the mutual short ranged interaction between nearby solid-melt interfaces. α is a dimensionless measure for the strength of the short range interaction [46].*

Peritectic phase diagrams are essential for many alloys and in particular for steels. We have studied different growth morphologies during **peritectic solidification**. We have investigated dendritic growth as a result of the peritectic reaction, and have compared this case to coupled cellular growth. The latter is of practical interest for the formation of composite materials directly during casting, as for example in Fe-Ni alloys. We find that depending on the spacing of the primary solidification, a morphological transition between dendritic and cellular growth occurs [49] (G. Boussinot, C. Hüter).

A new activity, which has been launched during the past years, is the modelling of **frictional phe-**

nomena (Fig. 9). Starting point is the well-known fact that the dynamic friction coefficient is typically velocity-dependent. The usual believe is that it is decaying with increasing velocity, as a result of the reduced time for micro-contact ageing. However, we have pointed out in an extended survey that many materials indeed show such a velocity weakening behaviour only at moderately low sliding speeds, whereas often a transition to a velocity strengthening regime at higher velocities, where the friction coefficient increases with speed, is rather the rule than the exception [50]. The appearance of a minimum frictional force in the transition regime has tremendous consequences for rupture fronts, which are travelling along a bi-material interface. In contrast to conventional "earthquake-like" events, which propagate essentially with the speed of sound, so called "slow fronts" with significantly lower velocities can emerge near the minimum of the frictional force [51]. Creep patches, which are a localized weakening of the micro-contacts at the interface under shear, often appear as precursors to these slow fronts, in agreement with recent laboratory observations of such periodic events [52]. Whereas the appearance of frictional instabilities on all scales from atomistic to geological dimensions is often attributed to a velocity-weakening behaviour, we recently found that also on the strengthening branch instabilities can occur for a strong bi-material contrast. The major difference between the two cases is that the latter is related to high frequency elastodynamic effects. The behaviour is expressed in terms of universal stability diagrams for large sample heights. In contrast, for thin samples (relative to the wavelength of the instability) waveguide-like modes can emerge, which are universally unstable [53] (M. Weikamp, R. Spatschek).

Several efforts have been made for the **development of phase field models** for mesoscale microstructure evolution modelling. The long-standing problem of thermodynamic consistency for phase field models with a thin interface limit for superior convergence behaviour has been solved. Here the antitrapping current prevents artificial solute segregation in the presence of a diffusional contrast between phases. It turns out, that a consistent model, which obeys the Onsager symmetries, also has to take into account proper off-diagonal cross couplings between concentration and phase fields for achieving realistic kinetics and to satisfy all boundary conditions. This also allows the elimination of spurious surface diffusion effects and temperature discontinuities at the interface (Kapitza jump) [54,-56]. Plastic effects and phase transformations induced by Joule heating by an external electrical field are considered in [57, 58], and additionally resulted in efficient implementations of the codes on graphics cards, which can accelerate the code by up to two orders of magnitude in comparison to a conventional CPU code (G. Boussinot, C. Hüter).

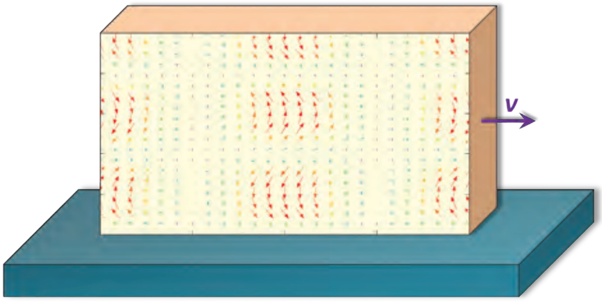


Fig. 9: *Frictional sliding on a rigid substrate with velocity v. For a thin slider waveguide like modes can form inside the slider and trigger a high frequency instability [53]. The displacement field of the standing waves is illustrated by the arrows.*

Defect Chemistry and Spectroscopy (C. Freysoldt)

This 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 oxides and insulating 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 [11]. Major challenges in the simulation arise from (1) 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, (2) from linking the microscopic picture to a coarse-grained theory that is able to describe the experimentally relevant time and length-scale (scale bridging), and (3) from developing useful approaches for point defects in alloys or amorphous materials.

The development of the **multi-scale programme package SPHInX** (available at http://sxlib.mpie.de) is a continuous activity of the group. A highlight from the past period is the extension of the MPI parallelization to automatic multi-loop parallelization in collaboration with the Max Planck Society Computing Centre in Garching and the exploration of optimizing the performance by hardware-specific (GPU = Graphic Processor Unit, AVX = Advanced Vector Extensions) algorithms for key functions. Further external collaborators on SPHInX development are S. Boeck (Gemmantics IT Consulting, Erkrath) and O. Marquardt (Paul-Drude-Institut, Berlin). Recent in-house developments cover the robust implementation of atomic-spin constraints (M. Grabowski) and a correction scheme for electrostatic interactions between defects at surfaces and interfaces.

Group III nitrides for optoelectronic device applications. To better understand the properties and growth of ternary nitride alloys, we study local ordering phenomena in epitaxially strained $In_xGa_{1-x}N$ layers and the associated finite-temperature thermodynamics by means of Monte-Carlo simulations (S. Lee). Our calculations predict the existence of a hitherto unknown ordered phase at 33% In composition [59]. An important problem for optoelectronic devices is the identification of loss mechanisms. The group has therefore worked on identifying which point defects may act as centres for non-radiative recombination (Y. Cui). Moreover, we worked on understanding the composition dependence of elastic and electronic properties of $In_xGa_{1-x}N$ layers grown on GaN [60, 61], as well as understanding the growth of GaN on Ge(111) as an alternative substrate [62] (Y. Cui) (Fig. 10). The methods developed here can be directly transferred to understand and predict orientation relationships of coherent precipitates or inclusions in structural materials such as steels.

A further area of interest has been to understand the role of **electrostatics** for atomic-scale simulations **at surfaces**, both for adsorbate-adsorbate interactions at metallic surfaces in collaboration with the group of M. Todorova [7], but also for charged defects at surfaces and interfaces, generalizing the Freysoldt-Neugebauer-van-de-Walle correction scheme for bulk defects to such systems.

Electrochemistry and Corrosion (M. Todorova)

The group aims to develop *ab-initio* based multiscale simulation techniques and apply them to problems in electrochemistry, with a strong focus on corrosion and related topics. The various activities in the group are tailored to provide in-depth insight into the functionality and evolvement of materials properties under the influence of the environment. Such insight will aid the **development of strategies to counteract, retard or suppress degradation phenomena in materials** (see p. 28).

As a first-step in this direction we have developed a unified approach that is based on a fully grand-canonical description of both ions and electrons and that connects and “translates” concepts in semiconductor defect chemistry and electrochemistry [63]. Our method links *ab initio* calculations quite naturally to experimental observables, such as the pH-scale and the electrode potential, which determine and characterise the state of an electrochemical system. It provides surprising new insight into apparently ”old” problems such as water stability, opens new routes to construct electrochemical phase (Pourbaix) diagrams and gives a handle to an absolute alignment of electrochemical potentials. The microscopic understanding gained makes it, furthermore, possible to obtain ion hydration/solvation energies by a hitherto not explored route. The developed approach provides a firm footing to the activities in the group, which are tailored to facilitate knowledge about the elementary process, important in the context of wet-electrochemistry, their interplay and specific corrosion related questions.

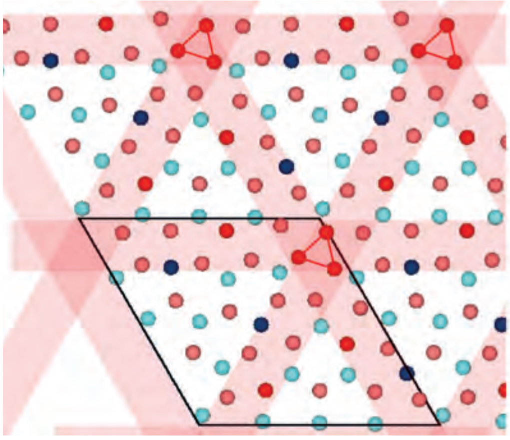


Fig. 10: *Calculated interface structure of a semicoherent Ge(111)/GaN(0001) interface with a 4:5 lattice match. Shown are the topmost Ge layers that translate the lattice match from 4 rows (Ge), in blue, to 5 rows (GaN), in red. The insertion of the extra rows (shaded stripes) are adopted by rebonding the tetrahedrally coordinated Ge atoms, leading to a small number of 5-fold coordinated Ge atoms. The model predicts interlayer separations in good agreement with experiment [62].*

The **interactions of atoms and molecules with surfaces** are at the onset of materials’ degradation mechanisms, such as **corrosion in reactive environments**. The investigation of the oxidation behaviour of Mg and Mg/Zn alloys by means of density functional theory calculations, is one example of research in this area (S.-T. Cheng). An interesting outcome is the high propensity of Mg to oxidise. Usually the adsorption of electronegative elements on metal surfaces leads to an increase in work function and a decrease in binding energy as the adsorbate coverage rises. A decrease in work-function and an increase in binding energy, i.e. the opposite behaviour, is observed for N, O and F on Mg(0001). Analyses of the electronic structure shows that this unusual adsorption behaviour is a consequence of a highly polarisable electron spill-out present in front of the Mg(0001) surface, which is responsible for the appearance of a hitherto unknown net-attractive lateral electrostatic interaction between same charged adsorbates (Fig. 11). Understanding this novel type of bonding allows us to rationalise the high propen-

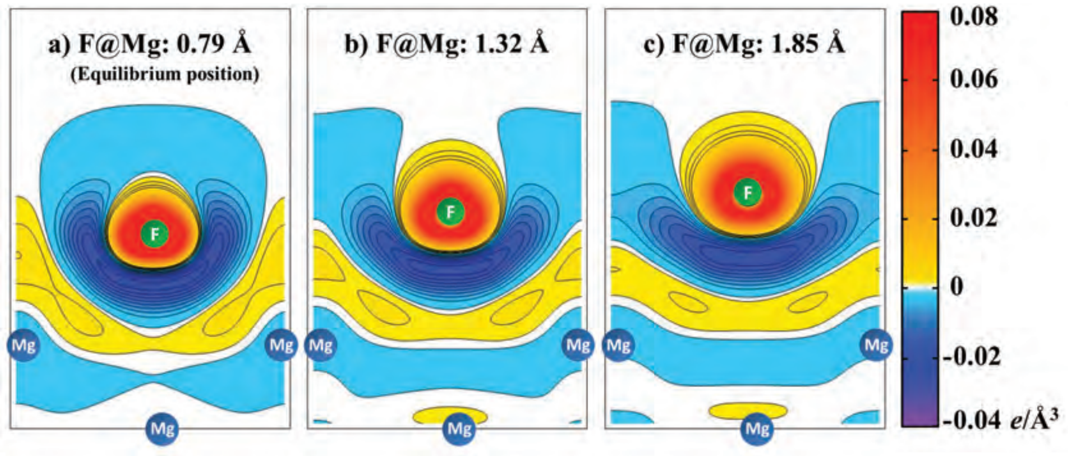


Fig. 11: *Difference electron density plots for 0.25 mono-layers of F adsorbed at different heights above the Mg(0001) surface. It visualizes the efficient embedding of F at its equilibrium adsorption position within the spill-out electron region of the surface, which facilitates the attractive interaction between the same charged adsorbates.*

sity of magnesium to corrode and get insight into the initial stages of corrosion - the arising attractive interactions lead to a spatial localisation of reactive atoms, which results in an earlier onset of oxidation at a given adsorbate's chemical potential [7].

Another example investigating the interactions of H_2S with Fe-surfaces (M. Ilhan) in the context of sour-gas corrosion is highlighted in p. 165.

An important step towards the modelling of, e.g., **metal dissolution or wet corrosion** is the ability to accurately describe ions and their solvation shells at the solid/liquid interface, within its proximity and within the bulk solution of an electrolyte. Studying ions near the interface requires including electric fields, the interaction with a (charged) surface, possible ion or field induced surface reconstructions. A realistic description of these phenomena and their interplay requires substantial new method developments which are underway or will be addressed in forthcoming investigations. The case of ions in bulk electrolyte is seemingly "easier" to tackle and provides one advantage – it allows us to gauge and develop our methodology by comparing calculated quantities to measurable observables. In this context systematic studies performed by A. Vatti present an important milestone. His investigations on the influence of various parameters (e.g. temperature, pressure, water surface dipole, DFT-functional) on the formation energies of ions in water allow us to access the importance of different contributions and to develop a protocol to calculated accurate ion formation energies (Fig. 12). It, furthermore, enables us to consolidate the approach usually used within the chemical/biological community, in which an ion in vacuum is considered the reference state for ion solvation, and the semiconductor based approach employed by us, in which the elemental state of the atom is considered the reference. A comparison of the calculated formation energies and transition levels for the investigated ions Cl, I, Br and Zn ions are found to accurately reproduce the experimental values. Hereby methodologies, such as the Freysoldt-Neugebauer-van-de-Walle correction scheme, developed for charged defects in semiconductors are of central importance.

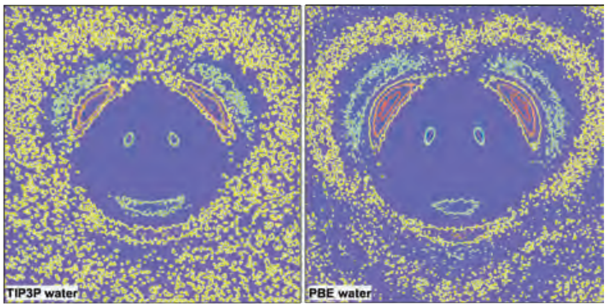


Fig. 12: *2D radial distribution function of water, which visualizes density variations as a function of distance from a chosen oxygen atom, obtained by molecular dynamic simulations with the popular classical potential (TIP3P) and the PBE exchange-correlation functional, which is known to overstructure water.*

A process which can be either utilised (i.e. to enhance the speed of drilling) or presents severe problems (i.e. cause major incidents in industrial plants) in industrial applications is **liquid metal embrittlement**. The liquid metal embrittlement of Fe by Zn [64] was studied in collaboration with K.-D. Bauer and K. Hingerl (Linz University, Austria). Evaluating the difference between the DFT-calculated grain boundary and the surface energies of the corresponding surfaces by utilising both the canonical Griffith and the grand-canonical Wang-Rice model showed that the Zn induced weakening of the GB sets in in the Wang-Rice formulation for Zn concentrations which are 2-3 orders of magnitude lower than in the Griffith case. Since the Wang-Rice model assumes sufficiently mobile Zn, which is able to preserve a constant Zn chemical potential at the crack tip as the crack propagates, and the canonical model assumes that the Zn amount present within the GB is preserved at the surface, i.e. it remains unchanged, this suggests that kinetic barriers in Zn diffusion can largely reduce the undesired effect of GB weakening. The attempt to combine the insights obtained from DFT based modelling with the continuum models employed and developed in the group of R. Spatschek is the topic of an ongoing project of the MPIE doctoral programme SurMat (P. Bhogireddy).

Further activities in the group focus on the stability of surfaces, interfaces or materials under the influence of the environment. The **identification of stable and metastable surface/interface structure subject to the given environmental conditions** is aided by the construction of surface Pourbaix diagrams. One example is our continuing work on the stability on polar ZnO(0001)-Zn surfaces, in which we focus on the interface phases in an aqueous electrolyte (S. Yoo). These provide the basis for comparison to experimental measurements performed in the groups of M. Valtiner (GO) and K. Morgenstern (Ruhr University Bochum). A further example are the **investigations of materials stability, understanding of stabilisation/destabilisation mechanisms and oxide growth** related to the construction of defect-phase diagrams [65, 5]. Such diagrams identify the majority defect species as functions of applied bias and chemical potential and allow discussions about the impact that aqueous electrolyte has on the electronic structure of a semiconducting electrode, thus providing insight into areas of interest in the context of electrochemical applications, such as corrosion. (see p. 161).

Growth Modelling (L. Lymperakis)

The focus of the growth modelling project group is on the epitaxial growth of compound semiconductors with a strong focus on III-Nitride materials. The topics of interest include the thermodynamics and kinetics of epitaxial growth [8, 66, 67], the electronic properties of surfaces [68, 69] and extended defects [70], as well as the growth and optoelectronic properties of semiconductor nanostructures [71]. Within the reported period L. Lymperakis was and is active in three EU funded projects: (i) The Industry-Academia Marie-Curie project SINOPLE, (ii) the Nanosciences, Nanotechnologies, Materials and new Production Technologies project ALIGHT, and (iii) ECSEL Joined Undertaking project PowerBase. Selected topics that were and are addressed in this area are:

The **growth of high In content InGaN alloys** with sufficiently high crystal quality constitutes a puzzling situation where the complex interplay between surface morphologies, partial pressures and growth temperature plays a central role. We have investigated the bulk and surface thermodynamics of $In_xGa_{1-x}N$ growth for the technologically relevant (0001) and (0 0 0 $\bar{1}$) growth planes by means of DFT calculations. Our calculations reveal that chemical effects (i.e. stronger Ga-N as compared to In-N bonds) result in a strong driving force for In surface segregation in the (0001) growth [8]. Furthermore, the thermal stability of excess In is found to be remarkably higher on N-polar surfaces than on the Ga-polar surfaces, indicating that for a given level of In incorporation, higher temperatures can be used for N-polar growth as compared to Ga-polar growth [67]. We have furthermore investigated the thermodynamics of solid and gas phases in molecular beam epitaxy like growth conditions and we highlighted the effect that plasma discharges have on the critical temperatures for InGaN decomposition: The weaker binding of the active nitrogen species produced by plasma as compared to ground state molecular nitrogen shifts the equilibrium and thus the maximum allowed growth temperatures to ≈500K higher values. However, the aforementioned temperatures have to be decreased by ≈100K for every 25% InN added to the InGaN alloy (A. Duff).

Surfactants and antisurfactants are species, deposited prior to growth on the substrate to overcome fundamental limitations set by thermodynamics and adatom kinetics in a particular heteroepitaxial system. The role and mechanisms of surfactants and self-surfactants in the growth of group III-Nitrides is well established and understood. However, the physics governing the technological important example of Si as antisurfactant in GaN was under intensive debate. In contrast to surfactants that mainly modify the growth mode by influencing adatom kinetics, we have revealed that antisurfactants modify the chemical potentials at the surface. This is based on the formation of a single $SiGaN_3$ subsurface monolayer (Fig. 13) that is **electrically active** and introduces a dipole moment caused by a charge transfer from the aforementioned layer to the surface [66]. Hence, growth proceeds in a lateral epitaxial overgrowth way only at locations where the $SiGaN_3$ layer is not present and allows to block and reduce the density of threading dislocations (in cooperation with M. Albrecht, Leibniz Institute for Crystal Growth, Berlin). Dislocations are extended defects that induce electronic states into the bandgap of semiconductors. However, a particularly interesting case is the **perfect screw dislocations** in a direct band gap semiconductor: The core of the defect consists of fully coordinated atoms and exhibits in first order a pure shear strain field. Thus, apart from their technological importance, these defects allow to investigate the physics underlying the effect of **shear strains on the electronic structure of semiconductors**. In order to investigate the later we developed an ***ab-initio* based**

quasi-continuum approach which combines DFT calculations with elasticity theory and we investigated the electronic properties of *a*-type screw dislocations in GaN [70]. In contrast to the common picture of exciton localization by screw dislocations, our analysis revealed that both the valence band maximum as well as the *s*-type, and hence in principle insensitive to shear strains, conduction band minimum (CBM) bend into the bandgap. This unexpected and with previous concepts not understandable downward shift of the CBM was shown to be a consequence of higher lying conduction bands that have *p* character and that are due to the huge strain fields around screw dislocations in GaN so strongly shifted that they hybridize with the band edge (in cooperation with M. Albrecht, Leibniz Institute for Crystal Growth, Berlin).

Wulff diagrams constitute a powerful tool to understand and control homo- and hetero-epitaxy along various crystallographic orientations and can be used to predict and design the growth of thermodynamically stable surface morphologies. However, due to the low point-group symmetry of the wurtzite crystal structure, polar and semipolar surface energies of these crystals are ill defined. Nevertheless, by invoking the similarities between the wurtzite {0001} and zincblende {111} planes, surface energies of the former can be calculated. Our calculations revealed that under typical GaN MBE (molecular beam epitaxy) growth conditions, the surface energies are independent of surface orientation and the mechanism to minimize the surface energy is to minimize the surface area. However, for the industry preferred HVPE (hydride vapour phase epitaxy) and MOCVD (metal organic chemical vapor deposition) growth, the surface energies show a strong orientation dependence having deep cusps at the polar (0001), non-polar (1 1 $\bar{2}$ 0) and the semipolar (1 1 $\bar{2}$ 2) orientation. This indicates that other semipolar (1 1 $\bar{2}$ *l*) orientations under conditions of thermodynamic equilibrium are prone to roughening and/or faceting towards the aforementioned planes. In a PhD project that started in January 2015 the **electronic properties and thermodynamics of point defects in oxide- and organometallic- perovskites** are investigated. $SrTiO_3$ constitutes a representative model for the wide class of large bandgap perovskites and has attracted considerable attention due to the two-dimensional electron gas (2DEG) observed at the interface with $LaAlO_3$ as well as due to the strong photocatalytic property under ultraviolet light. Halide perovskites are under an unprecedented progress thanks to their remarkably high efficiency in solar cell applications. In the first period the focus of the project is on the thermodynamics and electronic properties of oxygen single and di-vacancies in $SrTiO_3$ which are investigated by means of hybrid functional calculations. In the second period the focus will shift to inorganic-organic hybrid perovskite materials (M. Alam, in collaboration with MA and SN).

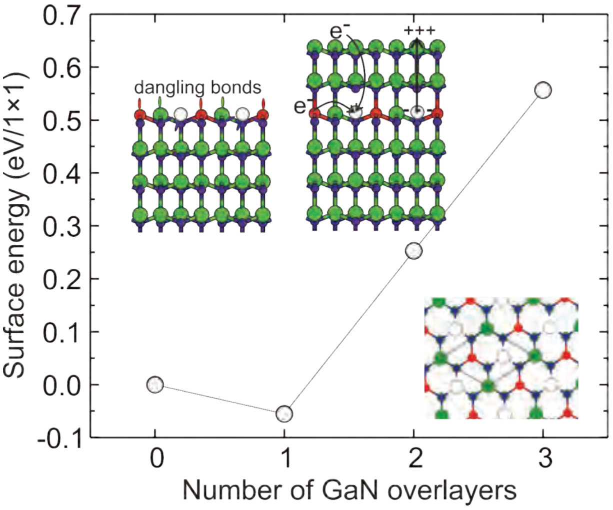


Fig. 13: *Surface energies, referenced with respect to the $SiGaN_3$ terminated surface, as function of the number of GaN overlayers grown above the $SiGaN_3$ layer. The upper insets represent the atomic configurations without and with two GaN overlayers, respectively. In the case of 2 GaN overlayers the charge transfer and the build in electrical dipole moment are indicated. The bottom inset represents a top view of the $SiGaN_3$ layer. The dashed frame indicates the $\sqrt{3}\times\sqrt{3}R30^o$ construction. Green, blue, red, and white balls indicate Ga, N, Si atoms and Ga vacancies, respectively. Figure taken from Ref. [66].*

References

1. Neugebauer, J.; Hickel, T.: WIREs Comput Mol Sci 3 (2013) 438-48.
2. Körmann, F; Grabowski, B.; Dutta, B.; Hickel, T.; Mauger, L.; Fultz, B., Neugebauer, J.: Phys. Rev. Lett. 113 (2014) 165503.
3. Glensk, A.; Grabowski, B.; Hickel, T.; Neugebauer, J.: Phys. Rev. Lett. 114 (2015) 195901.
4. Glensk, A.; Grabowski, B.; Hickel, T.; Neugebauer, J.: Phys. Rev. X 4 (2014) 011018.
5. Todorova, M.; Neugebauer J.: Farrad. Disc.180 (2015) 97.
6. Leyson, G.P.M.; Grabowski B.; Neugebauer J.: Acta Mater. 89 (2015) 50-59.
7. Cheng, S.-T.; Todorova, M.; Freysoldt, C.; Neugebauer, J.: Phys. Rev. Lett. 113 (2014) 136102.
8. Duff, A. I.; Lymperakis, L.; Neugebauer, J.: Phys. Rev. B 89 (2014) 085307.
9. Aydin, U.: PhD thesis (Paderborn, *to be submitted* in 2015).
10. Gupta, A.: Master thesis (Bochum, 2015).
11. Freysoldt, C.; Grabowski, B.; Hickel, T.; Neugebauer, J.; Kresse, G.; Janotti, A.; Van de Walle, C.G.: Rev. Mod. Phys. 86 (2014) 253.
12. Körmann, F.; Al Hasan Breidi, A.; Dudarev, S.L.; Dupin, N.; Ghosh, G.; Hickel, T.; Korzhavyi, P.; Munoz, J.A.; Ohnuma, I.: Phys. Stat. Sol. (b) 251 (2014) 53-80.

13. Steinmetz, D.R.; Japel, T.; Wietbrock, B.; Eisenlohr, P.; Gutierrez-Urrutia, I.; Saeed-Akbari, A.; Hickel, T.; Roters, F.; Raabe, D.: Acta Mater. 61 (2013) 494-510.
14. Sandlöbes, S.; Pei, Z.; Friák, F.; Zhu, L.F.; Wang, F.; Zaefferer, S.; Raabe, D.; Neugebauer, J.: Acta Mater. 70 (2014) 92-104.
15. Hickel, T.; Kattner, U.R.; Fries, S.G.: Phys. Stat. Sol. B 251 (2014) 9–13.
16. Körmann, F.; Grabowski, B.; Söderlind, P.; Palumbo, M.; Fries, S.G.; Hickel, T.; Neugebauer, J.: J. Phys: Cond. Mat 25 (2013) 425401.
17. Dutta, B.; Hickel, T.; Entel, P.; Neugebauer, J.: J. Phase Equ. Diff. 35 (2014) 695-700.
18. Zhang, X.; Hickel, T.; Rogal, J.; Fähler, S.; Drautz, R.; Neugebauer, J.: Acta Mater. 99 (2015) 281–289.
19. Nazarov, R.; Hickel, T.; Neugebauer, J.: Phys. Rev. B 89 (2014) 144108.
20. Hickel, T.; Sandlöbes, S.; Marceau, R.K.W.; Dick, A.; Bleskov, I.; Neugebauer, J.; Raabe, D.: Acta Mater. 75 (2014) 147-155.
21. Rogal, J.; Divinski, S.V.; Finnis, M.W.; Glensk, A.; Neugebauer, J.; Perepezko, J.H.; Schuwalow, S.; Sluiter, M.H.F.; Sundman, B.: Phys. Stat. Sol. B 251 (2014) 97-129.
22. Körmann, F.; Hickel, T.; Neugebauer, J.: Curr. Opin. Solid State Mater. Sci. (2015), http://dx.doi.org/10.1016/j.cossms.2015.06.001.
23. Bleskov, I.; Hickel, T.; Ruban, A.; Neugebauer, J.: Impact of Local Magnetism on Stacking Fault Energies, *submitted* to Phys. Rev. B
24. Dutta, B.; Körmann, F.; Ghosh, S.; Hickel, T.; Sanyal, B.; Neugebauer, J.: Ab initio study of lattice dynamics in systems with magnetic disorder, *submitted* to Phys. Rev. B
25. Dutta, B.; Cakır, A.; Giacobbe, C.; Al-Zubi, A.; Hickel, T.; Acet, M.; Neugebauer, J.: Ab initio prediction of martensitic and intermartensitic phase boundaries in Ni-Mn-Ga, *submitted* to Phys. Rev. Lett.
26. Behler, A.; Teichert, N.; Dutta, B.; Waske, A.; Hickel, T.; Auge, A.; Hütten, A.; Eckert, J.: AIP Adv. 3 (2013) 122112.
27. Dutta, B.; Hickel, T.; Neugebauer, J.; Behler, C.; Fähler, S.; Behler, A.; Waske, A.; Teichert, N.; Schmalhorst, J.-M.; Hütten, A.: Phys. Stat. Sol. RRL 9 (2015) 321-325.
28. Millán, J.; Sandlöbes, S.; Al-Zubi, A.; Hickel, T.; Choi, P.; Neugebauer, J.; Ponge, D.; Raabe, D.: Acta Mater. 76 (2014) 94-105.
29. Sawada, H.; Kawakami, K.; Körmann, F.; Grabowski, B.; Hickel, T.; Neugebauer J.: Acta Mater. 102 (2016) 241-250.
30. Löffler, A.; Zendegani, A.; Gröbner, J.; Hampl, M.; Schmid-Fetzer, R.; Engelhardt, H.; Rettenmayr, M.; Körmann, F.; Hickel, T.; Neugebauer, J.: Quaternary Al-Cu-Mg-Si Q phase, *submitted* to J. Phase Equil. Diff.
31. Dey, P.; Nazarov, R.; Dutta, P.; Yao, M.; Herbig, M.; Friák, M.; Hickel, T.; Raabe, D.; Neugebauer, J.: Ab initio explanation of disorder and off-stoichiometry in Fe-Mn-Al-C kappa carbides, *submitted* to Phys. Rev. B
32. Güvenç, O.; Roters, F.; Hickel, T.; Bambach, M.: JOM 67 (2015) 120-128.
33. Di Stefano, D.; Nazarov, R.; Mrovec, M.; Hickel, T.; Neugebauer, J.: Phys. Rev. B (*in preparation*).
34. McEniry, E.J.; Hickel, T.; Neugebauer, J.: Ab initio investigations of hydrogen behaviour in cementite-containing microstructures, Phys. Rev. B (*in preparation*)
35. von Appen, J.; Dronskowski, R.; Chakrabarty, A.; Hickel, T.; Spatschek, R.; Neugebauer, J.: J. Comp. Chem. 35 (2014) 2239–2244.
36. Duff, A.I.; Davey, T.; Korbmacher, D.; Glensk, A.; Grabowski, B.; Neugebauer, J.; Finnis, M.W.: Phys. Rev. B 91 (2015) 214311.
37. Grabowski, B.; Wippermann, S.; Glensk, A.; Hickel, T.; Neugebauer, J.: Phys. Rev. B 91 (2015) 201103.
38. Grabowski B.; Tasan, C.: Self-healing metals, Advances in Polymer Sciences, in press (2015).
39. Hüter, C.; Lin, M.; Schicchi, D.; Hunkel, M.; Prahl, U.; Spatschek, R.: AIMS Materials Science 2 (2015) 319-345.
40. Hüter, C.; Nguyen, C.-D.; Spatschek, R.; Neugebauer, J.: Mod. Sci. Mat. Sci. Eng. 22 (2014) 034001.
41. Hüter, C.; Neugebauer, J.; Boussinot, G.; Svendsen, B.; Prahl, U.; Spatschek, R.: Modeling of grain boundary dynamics using amplitude equations, *accepted* for publication at Cont. Mech. Thermodyn. (arXiv:1407.4283).
42. Boussinot, G.; Schulz, R.; Hüter, C.; Brener, E.A.; Spatschek, R.: Eur. Phys. J. Special Topics 3 (2014) 527.
43. Boussinot, G.: Surface Science Letters 607 (2013) L1–L3.
44. Spatschek, R.; Adland, A.; Karma, A.: Phys. Rev. B 87 (2013) 024109.
45. Adland, A.; Karma, A.; Spatschek, R.; Buta, D.; Asta, M.: Phys. Rev. B. 87 (2013) 024110.
46. Hüter, C.; Twiste, F.; Brener, E.A.; Neugebauer, J.; Spatschek, R.: Phys. Rev. B 89 (2014) 224104.
47. Sai Pavan Kumar Bhogireddy, V.; Hüter, C.; Neugebauer, J.; Steinbach, I.; Karma, A.; Spatschek, R.: Phys. Rev. E 90 (2014) 012401.
48. Sai Pavan Kumar Bhogireddy, V.; Hüter, C.; Neugebauer, J.; Shchyglo, O.; Steinbach, I.; Spatschek, R.: From wetting to melting along grain boundaries using phase field and sharp interface methods, *accepted* at Comp. Mat. Sci. (arXiv:1412.2891).
49. Boussinot, G.; Hüter, C.; Spatschek, R.; Brener, E.A.: Acta Mat. 75 (2014) 212.
50. Bar-Sinai, Y.; Spatschek, R.; Brener, E.A.; Bouchbinder, E.: J. Geophys. Res.: Solid Earth 119 (2014) 1738.

51. Bar-Sinai, Y.; Spatschek, R.; Brener, E.A.; Bouchbinder, E.: Scientific Reports 5 (2015) 7841.
52. Bar-Sinai, Y.; Spatschek, R.; Brener, E.A.; Bouchbinder, E.: Phys. Rev. E 88 (2013) 060403.
53. Brener, E.A.; Weikamp, M.; Spatschek, R.; Bar-Sinai, Y.; Bouchbinder E.: Dynamic instabilities of frictional sliding at a bimaterial interface, *submitted* for publication (arXiv: 1507.00156).
54. Boussinot, G.; Brener, E.A.; Hüter, C.; Spatschek, R.: Elimination of surface diffusion in the non-diagonal phase field model, *accepted* for publication (arXiv: 1411.0523).
55. Boussinot, G.; Brener, E.A.: Phys. Rev. E Rapid Comm 89 (2014) 060402(R).
56. Boussinot, G.; Brener, E.A.: Phys. Rev. E 88 (2013) 022406.
57. Monas, A.; Spatschek, R.; Hüter, C.; Tabatabaei, F.; Brener, E.A.; Apel, M.: J. Cryst. Growth 375 (2013) 39.
58. Spatschek, R.; Eidel, B.: Int. J. Solids Struct. 7 (2013) 2424.
59. Lee, S.; Freysoldt, C.; Neugebauer, J.: Phys. Rev. B 90 (2014) 245301.
60. Cui, Y.; Lee, S.; Freysoldt, C.; Neugebauer, J.: Phys. Rev. B 92 (2015) 085204.
61. Zhang, S.; Cui, Y.; Griffiths, J.T.; Fu, W.Y.; Freysoldt, C.; Neugebauer, J.; Humphreys, C.J.; Oliver, R.A.: Difference in linear polarization of biaxially-strained $In_xGa_{1-x}N$ alloys on non-polar a-plane and m-plane GaN, *submitted* to Phys. Rev. B.
62. Zhang, S.; Zhang, Y.; Cui, Y.; Freysoldt, C.; Neugebauer, J.; Lieten, R.R.; Barnard, J.S.; Humphreys, C.J.: Phys. Rev. Lett. 111 (2013) 256101.
63. Todorova M.; Neugebauer J., Phys. Rev. Appl. 1 (2014) 014001.
64. Bauer, K.-D.; Todorova, M.; Hinger, K.; Neugebauer J.: Acta Matter. 90 (2015) 69.
65. Todorova M.; Neugebauer J.: Surf. Sci. 631 (2015) 190.
66. Markurt, T.; Lymperakis, L.; Neugebauer, J.; Drechsel, P.; Stauss, P.; Schulz, T.; Remmele, T.; Grillo, V.; Rotunno, E.; Albrecht, M.: Phys. Rev. Lett. 110 (2013) 036103.
67. Duff, A.I.; Lymperakis, L.; Neugebauer, J.: Phys. Stat. Sol. (b) 252 (2015) 855.
68. Himmerlich, M.; Lymperakis, L.; Gutt, R.; Lorenz, P.; Neugebauer, J.; Krischok, S.: Phys. Rev. B 88 (2013) 125304.
69. Lymperakis, L.; Weidlich, P.H.; Eisele, H.; Schnedler, M.; Nys, J.P.; Grandidier, B.; Stiévenard, D.; Dunin-Borkowski, R.E.; Neugebauer, J.; Ebert, Ph.: Appl. Phys. Lett. 103 (2013) 152101.
70. Albrecht, M.; Lymperakis, L.; Neugebauer, J.: Phys. Rev. B 90 (2014) 241201.
71. Capiod, P.; Xu, T.; Nys, J.P.; Berthe, M.; Patriarche, G.; Lymperakis, L.; Neugebauer, J.; Caroff, P.; Dunin-Borkowski, R.E.; Ebert, P.; Grandidier, B.: Appl. Phys. Lett. 103 (2013) 122104.

Research Projects in Progress

Computational Phase Studies

Aydin, Hickel, Neugebauer: Chemical trends for the solubility of interstitials in metals using high-throughput calculations and machine learning

Begum, Dutta, Hickel: Monte-Carlo simulations of magnetic model Hamiltonians

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

Dey, Hickel (in collaboration with Z. Georgeou, F. Klose, Salzgitter Mannesmann Forschung GmbH): Impact of microstructure on hydrogen embrittlement in Cr-containing high-Mn steels

Dey, Hickel (in collaboration with B. Gehrmann, J. Klöwer, VDM Metals GmbH, Research & Development): Ab initio study on the interaction of hydrogen and microstructure in the alloys system 718

Dutta, Hickel (in collaboration with A. Hütten, A. Waske** (*Universität Bielefeld, **IFW Dresden)):* Coupling phenomena in magnetocaloric materials: From thin layers to composites

Dutta, Hickel (in collaboration with S. Ghosh, B. Sanyal** (*IIT Guwahati, India, **Uppsala University, Sweden)): Ab initio* study of lattice dynamics in systems with magnetic disorder

Glensk, Grabowski, Hickel, Neugebauer (in collaboration with B. Hallstedt, I. Egry**, 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

Glensk, Grabowski, Hickel, Neugebauer: Anharmonic contributions to *ab initio* computed thermodynamic material properties

Glensk, Grabowski, Hickel, Neugebauer (in collaboration with P. Neibecker and M. Leitner, Technische Universität München): Accurate determination of phonon linewidths

Gupta, Dutta, Hickel (in collaboration with S. Divinski, G. Wilde, Universität Münster): Mechano-chemical coupling during precipitate formation in Al-based alloys

Janßen, Hickel, Neugebauer: Automatized determination of error bars of *ab initio* derived quantities using the PyIron workbench

Janßen, Hickel, Neugebauer (in collaboration with C.C.Fu, F. Soisson*, H. Amara**, V. Pierron-Bohnes***, S. Divinski****, R. Drautz***** (*CEA Saclay, France, **LEM, France,***IPCMS Strasbourg, France, ****Uni Münster, *****Ruhr-Universität Bochum)):* Magnetism in iron alloys: thermodynamics, kinetics and defects

Körmann, Hickel, Neugebauer (in collaboration with M. Staadt, J. Rogal*, R. Drautz* (*ICAMS, Bochum)): Ab initio* simulation of magnetic contributions to the thermodynamics of metals

McEniry, Hickel (in collaboration with S. Merzlikin, T. Schablitzki**, J. Rogal**, R. Drautz**, O. Rott***, T. Pretorius*** (*GO department, **Ruhr university Bochum, **ThyssenKrupp Steel Europe AG)):* Experimental and atomistic analysis of thermal desorption spectroscopy (TDS) in steels

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

Sözen, Hickel, Neugebauer (in collaboration with L. Kunz, T. Eckl*, C. Elsässer* (*Robert Bosch GmbH, Applied Research, **Fraunhofer-Institut für Werkstoffmechanik IWM, Freiburg)): Ab initio* simulation of hard-magnetic materials

Zendegani, Körmann, Hickel (in collaboration with A. Ladines T. Hammerschmidt, R. Drautz (Ruhr-Universität Bochum)): Ab initio based calculation of the stability of selected TCP precipitates in steels: Temperature and interface effects

Zendegani, Körmann, Hickel, Neugebauer (in collaboration with B. Hallstedt, R. Schmid-Fetzer***, M. Rettenmayr*** (*RWTH Aachen, **TU Clausthal, ***U Jena)):* First-principles study of thermodynamic properties of the Q-phase in Al-Cu-Mg-Si

Zhang, Hickel, Neugebauer (in collaboration with J. Rogal and R. Drautz, Ruhr-Universität Bochum): Structural transformations in Fe-C alloys: From atomistic simulations to a microscopic understanding

Adaptive Structural Materials

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

Zhu, Grabowski, Neugebauer: *Ab initio* description of free energies of liquids

Maisel, Grabowski, Neugebauer: Coupling of vibrational free energies with the cluster expansion technique

Hadian, Grabowski, Neugebauer (in collaboration with C. Race, University of Manchester): Molecular dynamics simulations of grain boundary migration

Leyson, Grabowski, Neugebauer: Multiscale modeling of hydrogen enhanced homogeneous dislocation nucleation

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

Ko, Grabowski, Neugebauer (in collaboration J. Behler, Ruhr-Universität Bochum): Development of neural-network potentials for NiTi

Sahara, Grabowski, Neugebauer: Temperature dependent stacking-fault-energies in Co from *ab initio*

Alling, Grabowski, Glensk, Neugebauer (in collaboration F. Körmann, TU Delft and I. Abrikosov, Linköping University): Impact of lattice vibrations on electronic and magnetic properties of paramagnetic Fe

Glensk, Grabowski, Hickel, Neugebauer (in collaboration with P. Neibecker and M. Leitner, Technische Universität München): Accurate determination of phonon linewidths

Korbmacher, Grabowski, Neugebauer (in collaboration with A. Duff and M. Finnis, Imperial College London): Development of the TU-TILD method

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

Grabowski, Neugebauer (in collaboration with D. Ma, MA department and F. Körmann, TU Delft): Phase stabilities in high entropy alloys

Grabowski, Hickel, Neugebauer (in collaboration with F. Körmann, TU Delft, R. Reed, University of Birmingham, and A. Ruban, KTH Stockholm): Temperature dependent stacking-fault-energies in Al, Cu, and Ni from *ab initio*

Grabowski, Neugebauer (in collaboration with A. Ready and A. Sutton, Imperial College London): *Ab initio* description of point defects in Ti

Grabowski, Neugebauer (in collaboration with L. Huber, M. Militzer, J. Rottler, University of British Columbia, Vancouver): Concurrent QM/MM coupling in metals

Grabowski, Ko (in collaboration with C. Tasan, MA department): Self-healing metals

Grabowski, Korbmacher (in collaboration with B. Kaplan, KTH Stockholm and A. Blomqvist, Sandvik Company): Finite temperature **ab initio** calculated thermodynamic properties of orthorhombic Cr3C2

Grabowski (in collaboration with S. Bigdeli and M. Selleby, KTH Stockholm): *Ab initio* description of phase stabilities in Mn

Mesoscale Simulations

Spatschek, Neugebauer: Ab initio based mesoscale description of hydrogen embrittlement

Spatschek (in collaboration with A. Karma, and I. Steinbach**; *Northeastern University Boston, **Ruhr-Universität Bochum):* Grain boundary premelting

Spatschek (in collaboration with E.A. Brener, E. Bouchbinder**, *Forschungszentrum Jülich, **Weizmann Institute of Science, Rehovot, Israel):* Instabilities during frictional sliding

Spatschek (in collaboration with I. Steinbach, Ruhr-Universität Bochum): Liquid metal embrittlement

Spatschek (in collaboration with A. Monas, M. Apel**, E.A. Brener***, *ICAMS, Ruhr-Universität Bochum, **ACCESS Aachen, ***Forschungszentrum Jülich)*: Phase transformations with Joule heating

Spatschek (in collaboration with B. Eidel, Universität Siegen): Plastic effects on the kinetics of phase transformations

Spatschek (in collaboration with U. Prahl, M. Hunkel**, *IEHK, RWTH Aachen, **IWT Bremen):* Bainitic press hardening

Spatschek (in collaboration with G. Boussinot, E.A. Brener**, *ACCESS Aachen, **Research Center Jülich):* Peritectic solidification

Spatschek (in collaboration with M. Friák, Brno, Czech republic): Nonlinear elasticity

Spatschek (in collaboration with M. Finnis, Imperial College London): Phase field modeling of oxide scale growth

Defect Chemistry and Spectroscopy

M. Grabowski, Freysoldt, Neugebauer: Atomic spin constraints in density functional theory

Koprek, Freysoldt, Neugebauer: Element distribution at CdS/CIGS interfaces in solar cells

Freysoldt, Neugebauer (in collaboration with S. Zhang, University of Cambridge): Electronic properties of InGaN under finite strains

Freysoldt (in collaboration with K. Reuter, Garching Computing Center, Germany): Parallel algorithms for atomic orbital projections from plane-wave basis sets

Freysoldt, Neugebauer (in collaboration with C. Liebscher, SN): Electron spectroscopy of CuCr

Freysoldt, Neugebauer: Phonons in ionic systems

Electrochemistry and Corrosion Science

Cheng, Todorova, Friák, Neugebauer (in collaboration with M. Rohwerder, GO department): A density functional theory study on the oxidation behaviour of Mg and Mg-Zn alloys

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

Yoo, Todorova, Neugebauer (in collaboration with M. Valtiner, GO department and K. Morgenstern, RUB): Stability of electrode materials in an electrochemical environment

Surendralal, Todorova, Neugebauer: Machine-aided calculations of charged point defects in magnesium and iron oxides

Todorova, Neugebauer (in collaboration with L. Yang and S. Wippermann, GO department): Accurate hydration energies from *ab-initio* calculations

Growth Modelling

L. Lymperakis and J. Neugebauer (in collaboration with Infineon Technologies Austria AG): Identification and strategies to passivate efficiency limiting defects in GaN-based power electronics through *ab initio* simulations

L. Lymperakis, Ch. Freysoldt, S. Maisel, and J. Neugebauer, (in collaboration with M. Albrecht, IKZ, Berlin): *Ab-initio* based cluster expansion simulations of InGaN alloys

L. Lymperakis and J. Neugebauer (in collaboration with Ph. Ebert, Forschungszentrum Jülich): Electronic properties and energetics of novel nanostructures

L. Lymperakis and J. Neugebauer (in collaboration with M. Himmerlich and S. Krischok, TU Ilmenau): Electronic properties and thermodynamics of semiconductor surfaces

L. Lymperakis (in collaboration with A. Georgakilas, University of Crete, Greece): Growth of III-Nitride nanostructures

L. Lymperakis (in collaboration with E. Iliopoulos, University of Crete, Greece): InGaN alloys for photovoltaic applications

M. Alam, L. Lymperakis, and J. Neugebauer (in collaboration with MA and SN): Electronic properties and thermodynamics of point defects in oxide- and organometallic- perovskites

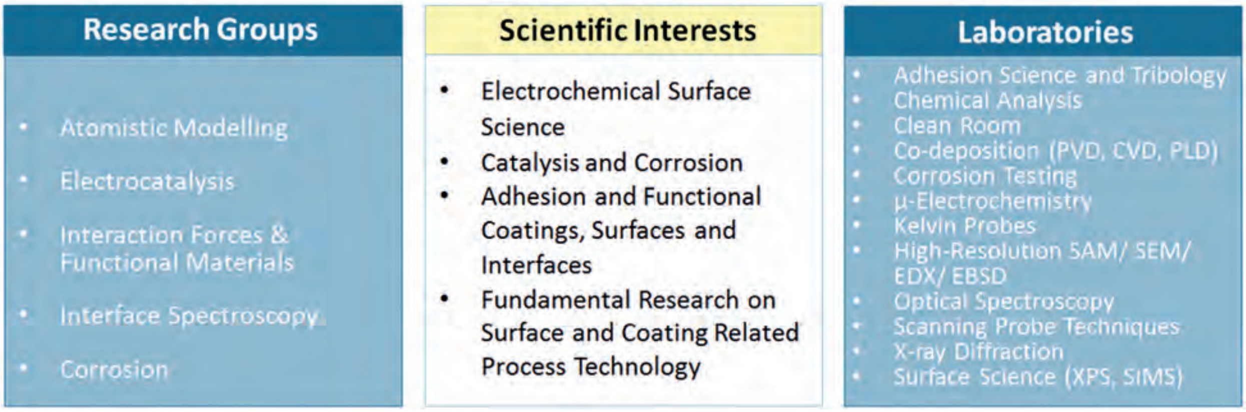
Department of Interface Chemistry and Surface Engineering

M. Rohwerder, M. Stratmann (provisional head J. Neugebauer)

Introduction

The Department of Interface Chemistry and Surface Engineering (GO) is mainly focussing **on corrosion and adhesion science as well as electrochemical energy conversion**. It is internationally known to be one of the leading groups in the field of electrochemical sciences. 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 and smart coatings amongst others. The department currently hosts five research groups. The different groups focus on high-throughput methods and the development of combinatorial methods in adhesion science and electrochemistry, on characterization of electrified interfaces by complementary methods such as vibrational spectroscopy, *in-situ* diffraction studies and scanning probe techniques, such as Scanning Flow Cell (SFC), Scanning Kelvin Probe (SKP), Atomic Force Microscopy (AFM) or Scanning Tunnelling Microscopy (STM), as well as on related *ab initio* simulation. We combine electrochemistry with a surface and interface science approach, and in most projects we complement both, experimental studies on atomically well-defined model systems as well as on technical systems with atomistic *ab initio* 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 reporting period the department was subject to a number of advancements and adjustments: First of all, in June 2014 the head of the department, Martin Stratmann, took over as president of the Max Planck Society and is officially on leave from his position at the MPIE. Michael Rohwerder took over the coordination of the department and Jörg Neugebauer (head of the department "Computational Materials Design") acts as temporary head of the department. In 2013 the department was able to gain Stefan Wippermann as head of a new research group on "Atomistic Modelling" (see p. 29). The motivation of this theory group located inside an experimental department is to gain atomic level insight into key processes in the gas-phase, in solutions, at interfaces/surfaces and in nanostructures, which are inaccessible by other means. Moreover, in 2013 Frank Renner (head of the former "Interface Structures and High Temperature Reactions" group) accepted a position as professor at the University of Hasselt and left the MPIE. In 2014 Michael Rohwerder was offered the position as full professor in the MSE department at the Ohio State University, but could be successfully kept at the Institute. The name of his research group was changed from "Molecular Structures and Surface Modification" to "Corrosion" to better cover the much broader current scope of this group. Furthermore, at the end



Research Groups

- Atomistic Modelling
- Electrocatalysis
- Interaction Forces & Functional Materials
- Interface Spectroscopy
- Corrosion

Scientific Interests

- Electrochemical Surface Science
- Catalysis and Corrosion
- Adhesion and Functional Coatings, Surfaces and Interfaces
- Fundamental Research on Surface and Coating Related Process Technology

Laboratories

- 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 portfolio and expertise.*

Fig. 2: *The GO (summer 2013).*

of 2014 the Christian-Doppler-Laboratory (CDL) for Diffusion and Segregation during Production of High Strength Steel Sheet (group head: Michael Rohwerder), which was established in 2008, was concluded after seven successful years.

The department is actively participating in various collaborative research efforts with internal and external partners. Several scientists of the department are taking part in the DFG Cluster of Excellence „Ruhr Explores Solvation“ (RESOLV), which is centred at Ruhr University Bochum‘s (RUB) Faculty of Chemistry and Biochemistry. Our contributions to solvation science in RESOLV focus on the role of solvents in electrochemical reactions, and solvation of interfaces. Further, the GO is part of the EU 7th framework programme Marie Curie Initial Training Network (ITN) project „Somatai - Soft Matter at Aqueous Interfaces, which started in October 2013.

With its versatile experimental and theoretical expertise (Fig. 1) the GO is in the unique position to assist and promote diverse **industrial research by its profound expertise in investigating the 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 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. In the reporting period besides ORR also the oxygen evolution reaction (OER) has become object of intense research activities and in this context also research on transpassivity of electrode materials under OER conditions. The knowledge obtained in the fundamental research on electrochemical key reactions such as oxygen reduction and oxygen evolution plays a crucial role in helping us to unravel practical problems met in industrial applications or processes such as in corrosion, batteries and fuel cells.

Several research projects focus on industrial processes such as electrophoretic coating, phosphating, alternative surface treatments. 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. A special collaborative interest of the institute is hydrogen in steel. The activities in this field have been further enhanced, complementing experimental and theoretical methods in cooperation between the departments play an important role. In the GO in particular the Scanning Kelvin Probe and Scanning Kelvin Probe Force Microscopy were further developed in combination with complementing techniques to uniquely and directly detect hydrogen in steel with high spatial resolution (see p. 39).

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 over-potential that limits the energy efficiency. One important approach for advancing our understanding of this reaction is to make progress in *ab initio* simulations about it. This is, however, difficult, because reliable experimental *in situ* data for instance of reaction products are difficult to obtain and thus experimental feedback is more or less missing. To overcome this problem dedicated model experiments were designed. By combining electrochemical experiments with attenuated total reflection infrared absorption spectroscopy, the mechanism of the electrochemical oxygen reduction reaction on n-Ge(100) as a model semiconductor has been investigated. Surface-bound superoxide and peroxide have been found as intermediates both in acidic and alkaline electrolytes. Peroxide is more prominent in alkaline solutions. For the assignment of the vibrational spectra, **a combination of density functional theory (DFT) calculations and isotope exchange experiments was used** [1-2]. Especially in acidic solution, the onset of the oxygen reduction is closely linked to a change in surface termination to an H-terminated surface at negative electrode potentials. On the basis of several experimental datasets, **a catalytic cycle for the ORR on Ge(100) was suggested** [1]. Analysing the relation between absorbance of certain intermediates and total current opens the way for a detailed understanding of the kinetics of individual steps in this multistep reaction [2-4].

In collaboration with the group of P. Koelsch (Karlsruhe Institute of Technology / University of Washington, Seattle), who is an expert on sum frequency generation (SFG) spectroscopy, *in situ* electrochemical SFG experiments on electrode surfaces modified by molecularly highly ordered araliphatic self-assembled monolayers have shown third-order nonlinear optical effects, i.e. a coupling of the static electric field to the vibrational transitions [5]. **Such a coupling may be exploited to probe the electric field at the electrode/electrolyte interface**, if there is a method (e.g. by first principles calculations) to quantify the coupling coefficient. The molecular structure of this electrode/electrolyte interface is essential in electrochemical and natural processes. In particular, ion and water structuring at charged solid/electrolyte interfaces dominate structure and functionality in many physiological, geological, and technological systems. In technological applications and processes ion concentration ranges often above 50-100 mM where structuring is expected to occur within the range of molecular dimensions. Y**et no qualitative or quantitative model exists for predicting ion structuring at solid/liquid interfaces**. In the recent years, we started to use force probe experiments as workhorse to directly probe structural forces at solid/liquid interfaces. For instance we showed how specific ion adsorption can strongly influence how electric charge is compensated in the electric double layer on model ceramic surfaces [6]. These studies are planned to be complemented by experiments with the recently installed Near-Atmospheric-Pressure Photoelectron Spectroscopy (NAP-XPS). The **NAP-XPS** is a new instrument in the department and has now been integrated into a dedicated environment for fundamental research on electrochemical sciences, partly in cooperation with the excellence cluster RESOLV.

Also interfacial structuring of organic electrolytes, including r**oom temperature ionic liquids (RTILs) and Li-ion battery fluids**, was studied. RTILs have emerged as unique electrolytes for energy applications offering potential for designable chemical and physical properties. How ionic liquids structure at charged interfaces determines the functionality in electrochemical devices such as batteries or super capacitors.

Yet, the importance of impurities (water or other solutes) on molecular ion structuring and charging mechanism of solid interfaces in RTILs is unclear and has been largely ignored. Impurities may alter structures, charging characteristics, and hence performance at electrified solid in both a positive or negative way. In the reporting period **force probe experiments and XPS measurements** were utilized to directly measure how water and other impurities alter the interfacial structuring and charging characteristics of RTILs on dielectric surfaces and electrified metal surfaces [7]. On ceramic interfaces water can dissolve surface-bound cations, which leads to high surface charging and strong RTIL layering. In contrast, layering of dry RTIL at weakly charged mica surfaces is weakly structured. At electrified gold electrodes the influence of water is limited to interactions within the RTIL layers, and is not related to a direct electro-sorption of water on the polarized electrode. Currently, the influence of other potentially beneficial additives such as organic long-chained molecules and polymer materials is tested. Generating such detailed insights into molecular interface structures will further guide the targeted development of structures and properties at electrified interfaces.

Another important aspect is **how electric double layers respond dynamically during active operation** of an electrochemical device, or during ongoing active corrosive processes that continuously generate or deplete charge at an interface. To study such dynamic aspects of electric double layers we also utilized direct electric double layer force measurements. For the first time we could directly measure strong electrochemical reaction forces, which are due to temporary charge imbalance in the electric double layers caused by depletion/generation of charged species. The real-time capability of our approach revealed significant time lags between electron transfer, oxide reduction/oxidation, and solution side reaction during a progressing electrode process. Comparing the kinetics of solution and metal side responses provided unique evidence that noble metal oxide reduction proceeds via a hydrogen adsorption and subsequent dissolution/re-deposition mechanism [8]. In addition, the existence of reactive forces may explain why adhesive and cohesive forces can trigger processes such as crevice corrosion or stress corrosion cracking and nano-particle from electrode support materials.

Many of the research projects allocated in the field of electrochemical sciences are closely related to the DFG-funded Cluster of Excellence RESOLV. More specific current research within RESOLV is, among other activities, focussed on electrochemistry in the “dry” (see further below) and on *in situ* vibrational spectroscopy, with the aim on the understanding of the electrode-potential dependent solvation of electrodes [9]. Main aim is again to link experimental results to first principles calculations.

Corrosion

The corrosion research of the department includes aqueous, atmospheric and bio-corrosion processes and their inhibition, covering both fundamental and applied aspects.

Using the scanning flow cell (SFC) system with downstream analytics allows **electrochemical high-throughput screening and characterization of corrosion properties of material samples**. This method, which was developed in the GO, has become a routine technique for corrosion research and up to now 8 set-ups with integrated mass spectroscopy or UV-vis analysis are in operation. In the reporting period SFC was successfully applied for studying the corrosion of magnesium, where it provided important insights, including the much disputed negative difference effect [10-11]. In extension, current efforts include the investigation of various material libraries, which should finally lead to guidelines for the optimization of material composition for best corrosion protection with regard to the respective environment of use.

Of special importance of our research is the corrosion behaviour of zinc (alloy) coatings. Despite the high importance in corrosion protection, the fundamental understanding of the behaviour of zinc based metallic coatings under different and often changing environmental conditions is still not exhaustive. Therefore, the in-house developed SFC high throughput approach coupled to online analytics, which is capable to deal with the issue of the complex interrelation between many material parameters and simulated test conditions efficiently, has been in particular extended for the variation of electrolyte composition. This has been utilized in collaboration with industrial partners to increase our understanding of the impact of the electrolyte components on the fundamental corrosion mechanism and kinetics of Zn based systems [12]. Moreover, the SFC has been successfully installed in the laboratories of the collaboration partners, and is being further technically optimized so that it can become a routine tool for the evaluation of corrosion properties also in other industrial laboratories.

The investigations by SFC are mainly focused on the fundamental dissolution kinetics. The **longterm corrosion performance** of zinc alloy coatings is, however, to great extent also determined by the corrosion product layers forming over time. These were in focus of research, too. Important information on the effect of environmental factors and the role of the micro-structure could be elaborated [13-16]. Moreover, also the **initial stages** of Zn corrosion are of importance, as they may influence the further course of corrosion. Electrochemically grown oxides on zinc are the first corrosion products. A combination of ex situ and *in situ* analysis of the oxidation of zinc in carbonate shows that the oxide films growing are significantly different from bulk oxides, as e.g. detected via their Raman and photoluminescence spectrum. The reason is the large density of defects in these oxides [17]. On copper, oxide growth in solution has implications for the antibacterial activity of the copper surfaces, as studied in collaboration with F. Mücklich, Chair of Functional Materials of the Saarland University [18]; however, these are non-trivial effects that require further model experiments.

The corrosion of metallic alloys, especially steels, in the presence of aqueous H_2S, so-called **“sour gas corrosion”**, is an old topic in corrosion research that surfaces again because of the exploitation of more and more non-classical sources of oil and gas. When reviewing the literature, one notices a lot of reports based on field experience and standardised tests, but there is still a limited understanding of a number of fundamental aspects [19]. The limited understanding motivated collaboration with the steel industry to investigate in more detail mechanistic aspects of sour gas corrosion, e.g. the electrochemistry of iron in acidic electrolytes containing H2S. Interesting results show the metallic nature of the corrosion products, and a strong oxygen content in corrosion products, possibly caused by the presence of amorphous iron oxides [20]. The complex chemistry of iron sulfides and oxides, coupled with a complex electrochemistry makes sour gas corrosion hard to understand, and current efforts are directed to further progress in this direction.

Microbially influenced corrosion (MIC) by marine sulfate-reducing bacteria is a major contributor to corrosion of iron in anoxic environments [21]. Anaerobic MIC causes serious damages in the oil and gas industry, thus assessing and monitoring of corrosion problems and also elucidating the yet still unresolved corrosion mechanism is of great importance. In close cooperation with the Max Planck Institute for Marine Microbiology in Bremen and in a multidisciplinary approach utilizing electrochemical techniques, surface analytics and molecular biological methods, we succeeded in quantifying corrosion rates *in-situ* [22] and gaining a more detailed insight into the fundamental electron transfer mechanism at the electrode/bacteria interface [23-24]. More recently, we have also shown that the direct electron transfer mechanism also proceeds in other bacterial cultures, in particular methanogenic lithoautotrophic archaeon, which makes them highly active and selective in the conversion of CO_2 to CH_4, a topic also of great importance in energy conversion [25].

Crevice corrosion (CC) of metals remains a serious concern for structural materials and aerospace engineering. Yet a **real-time *in situ* visualization of corrosion, and its inhibition within a confined geometry**, remains challenging. In our department we recently demonstrated how white light interferometry (WLI) can be utilized to directly visualize corrosion processes in real-time, *in-situ* in a confined (i.e. buried) geometry [26]. We studied in detail how pure **aluminum corrodes in crevice geometries and how vanadate ions can effectively inhibit CC of aluminum**. As shown in Fig. 3 (a) corrosive 5 mM NaCl solution is sandwiched between the aluminum oxide and an opposing crevice former surface (mica) to form a confined zone. Simultaneously WLI directly reveals the shape of a confined crevice area in terms of fringes of equal chromatic order (FECO) – shown in the panels above the schematic. A FECO is a standing wave that reflects back and forth between the corroding aluminum surface and the inert probe mirror located behind the crevice former (mica). After 1.5 and 2 hours, Fig. 3 (b-c), clearly show that regions just outside the intimate contact area show first signs of corrosion (increased light intensity). Interestingly, CC does not initiate at the intimate contact zone but just outside, where the electrolyte layer above the Al is about 20-200 nm thick. This behaviour indicates a delicate balance between the established corrosive potential within the confined zone and material transport rates out of/ into the confined zone. Fig. 3

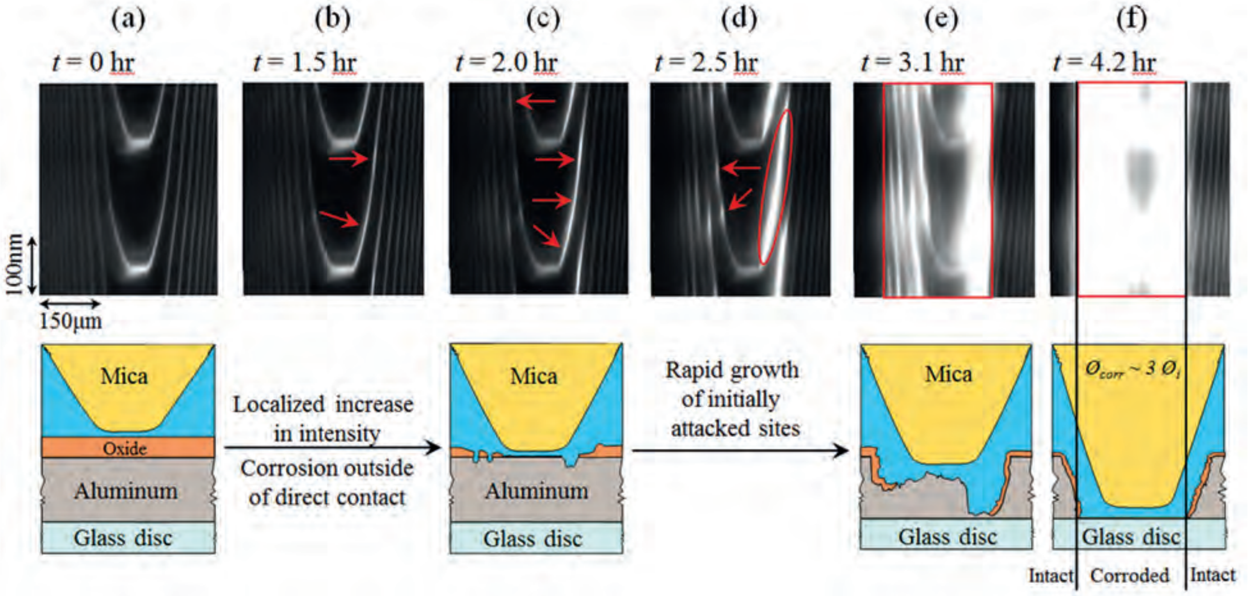


Fig. 3: *Consecutive 2D FECO images obtained as a function of time after injection of 5 mM NaCl into a confined aluminum/mica contact. The schematics below show progress of the corrosive reaction as deduced from the FECO images. As indicated in the schematic shown in (c) a subtle balance between material transport rates (diffusion and migration) as well as reaction rates may control the locations where rapid Crevice Corrosion initiation is most likely [26].*

(d-e) show how the confined zone rapidly corrodes until the corroded area is about three-times the initial intimate contact area. Using this method we could directly quantify (1) critical bulk concentrations of the corroding species (chloride) that are necessary to initiate CC; (2) the concentration of corrosion inhibitor above or below which the corrosion is effectively inhibited For instance, 2.5 mM NaVO3 can effectively inhibit the corrosion of aluminum in 5mM NaCl solutions for 25 hours, however, in 50 mM NaCl the rapid breakdown of the native oxides occurred after about three hours. (3) In general we could show that CC initiates with a breakdown of the passivating oxide surface. This method now allows for a detailed and high throughput screening of effective corrosion inhibitors.

Such a real-time Angstrom-resolved **visualization of dynamic processes at electrified solid/liquid interfaces** has not been feasible to date. We recently also reported a unique experimental setup that allows us to generate a real-time atomistic view into dynamic processes at electrochemically active metal interfaces using white light interferometry (WLI). Quantitative *in situ* analysis of the potentiodynamic electrochemical oxidation/reduction of noble metal surfaces shows that Angstrom thick oxides formed on Au and Pt are high-ik materials; that means, they are metallic or highly defect-rich semiconductors, while Pd forms a low-ik oxide. In contrast, under potentiostatic growth conditions, all noble metal oxides exhibit a low-ik behaviour [8]. This clearly demonstrated that surfaces under active conditions are very much different from equilibrated surfaces. Yet, exactly the dynamic aspects of growing or reducing oxide thin films are very important with respect to stability of metallic materials. With our new methods we can now for the first time aim to understand the molecular origin of actively progressing processes such as reactive dissolution of metals, in particular also in trans-passive regions, where passivation typically breaks down during dynamic change of the surface structure.

With respect to trans-passive degradation, the department combines a number of different techniques in order to study how and why oxides break down. This is becoming a topic of increasing importance for all research groups of the department who strongly cooperate on this topic.

High temperature oxidation is another topic that is becoming increasingly important within the GO. Special focus are short term high temperature treatments that are crucial in many industrial processing steps in steel making, such as hot rolling and recrystallization annealing before hot dip galvanizing. These relatively short processing steps are generally not much investigated yet and are determined by kinetics of oxygen uptake, nucleation and growth of oxides [27] and only to limited extent by diffusion, usually considered of key importance in high temperature oxidation, which leads to final morphologies that are still far from equilibrium. This research was originally part of the Christian Doppler Laboratory for Diffusion and Segregation during the Production of High Strength Steel Sheet (Michael Rohwerder) and will be continued in the Corrosion group.

Adhesion, thin films and friction

Organic coatings are commonly employed to protect materials surfaces against corrosion. On steel, including galvanised steel, cathodic delamination is the main mechanism of failure of these coatings. 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 expertizes of the department.**

Recent efforts have been made to understand the nature of the chemical reactions that occur in the process of cathodic delamination by preparation of synthetic model interfaces, mainly on zinc, that have been polymer coated and subjected to cathodic delamination. After deposition of ZnO sol gel films with different morphology on zinc surfaces, those morphologies with mainly low energy surfaces show slowest delamination of weakly bound polymer coatings, indicating that the destruction of the ZnO surface is important [28]. On the other hand, thin acrylate polymer films have been prepared in a free radical copolymerisation process where one co-monomer is bound to the zinc surface. Resulting reaction-controlled delamination rates depend e.g. on the content of hydrophobic cross linkers and the total crosslinker content, which implies that a role of radical intermediates of the ORR is likely in the delamination process [29]. *In situ* Raman monitoring of the initial stages of cathodic delamination on zinc under certain conditions shows oscillations in pH and amount of corrosion products. The observation of oscillations implies that anodes and cathodes must be correlated over the surface, as opposed to the current textbook picture of random locations [30].

The breaking of the covalent bond between gold and the sulphur atom of a self-assembled monolayer (SAM) may be regarded as one particular mechanism of de-adhesion. In general self-assembled monolayers can serve as model systems for studying degradation mechanisms as they might occur at buried interfaces. Hence, a number of self-assembled monolayers that could be of interest for further studies was investigated [31-32]. In a series of experiments of the reductive desorption of SAMs in a coupled ellipsometric – electrochemical experiment, araliphatic and alkyl SAMs with long chains have been found to remain intact or even adsorbed to the metal surface even after breakage of the covalent bond [33]. On the other hand, shorter thiols stabilise aggregates possibly containing hydrogen at the electrode/electrolyte interface [34]. Up to now one unsolved hindrance for a detailed study of fundamental investigation of cathodic delamination was that the oxygen reduction rate at the buried interface was not directly accessible. Based on combining Kelvin probe with a hydrogen permeation experiment, a novel methodology was developed which allows for the first time direct measurement of the oxygen reduction kinetics at the buried interface (see p. 38). Also of interest and of crucial importance for understanding delamination is the role of surface oxide terminations and studying its effect on the properties of the resulting interface with polymers [102]. Another important aspect of delamination is the mobility of charges along the buried interface. Hence, the study of charge mobility and of its dependence on crucial surface parameters such as OH termination is of great importance [103, 109].

In addition, unravelling the complexity of modern adhesives acting in the macroscopic world relies on understanding **the scaling of single molecular interactions towards integral macroscopic interactions**. In our department we recently developed a synergistic experimental approach which combines macroscopic adhesion measurements using a Surface-Forces-Apparatus and single molecule unbinding experiments using an Atomic-Force-Microscope (AFM) [35]. We developed a unique experimental framework to test the well-renowned Jarzynski's equality, which relates work performed under non-equilibrium conditions (in this case during single molecule unbinding in AFM) with equilibrium free energies, which are necessary to predict macroscopic interactions. In two case studies it has been shown that the equilibrated macroscopic work of adhesion scales linearly with the number density of interface bonds s as long as the chemical functionalities do not interact with each other laterally. Irrespective of how far from equilibrium single molecule experiments are performed, the Jarzynski's free energies converge to the same values as measured on a macroscopic scale. These results validate the applicability of Jarzynski's equality in general, and allow us now to unravel the scaling of non-equilibrium single molecule experiments to scenarios where a large number of bonds interacts simultaneously in equilibrium and at the macroscopic scale. Based on this we developed a scaling strategy that allows us to predict large-scale properties such as adhesion at electrified interfaces on the basis of single-molecule measurements (Interaction Forces and Functional Materials group) [36]. This now opens a new path to understand macroscopic adhesion and delamination.

Functional surfaces, interfaces and coatings

The development of **intelligent coatings for corrosion protection** within the department focuses to a significant extent on the application of conducting polymers and particle modified zinc coatings. While in the prior reporting period a thorough investigation of the problems involved with the use of conducting polymers for corrosion protection has been carried out in depth and solutions how to solve them were developed, in this reporting period further developments were made for a more efficient performance of so called intelligent self-healing coatings. One main success was the development of polyaniline capsules that can be loaded with inhibitors or other self-healing agents (together with partners from the Max Planck Institute for Polymer Research in Mainz) and first successful applications [37-38]. Another major break-through was the successful combination of a smart organic coating containing smart capsules loaded with monomer with a zinc coating containing capsules that were loaded with a catalyst [39]. For the first time a coating system could be demonstrated to case-sensitively release active agents upon onset of corrosion that closed a macroscopic defect site by formation of a new polymer coating.

Moreover, thin organic films have been exploited for surface **modification of metal surfaces**, combining innovative chemical synthesis in collaborating groups with high-level surface analysis at the MPIE. Salt-like Fe^{II} containing complexes were immobilised on gold via thiocyanate anchors in a collaborative work with A. Grohmann, Chair of Bioinorganic Chemistry, TU Berlin [40]. Phenothiazines as redoxactive components and as candidate materials for molecular electronics have been synthesised with phosphonate linkers in the Department of Organic Chemistry at the Heinrich Heine University Düsseldorf, headed by T.J.J. Müller. Such phenothiazines adsorb as monolayers to oxide-covered iron and as multilayers to oxide-covered zinc [41], which widens their spectrum of applications. Also, the classical gold-sulphur system still holds surprises when used with complex molecules, e.g. azobenzene derivatives. Ordered films with different adsorption geometries have been obtained here, depending on the precursor, but with same chemical composition [42].

Besides their role in corrosion and corrosion protection, particular in passivity, semiconducting oxides are also interesting for a number of other applications, e.g. in **photovoltaics, photocatalysis and in sensing**. For a fundamental understanding of the role and nature of defects as well as the band alignment, advanced photoemission spectroscopy experiments in ultrahigh vacuum have been conducted in collaboration with M. Krzywiecki from the Silesian University of Technology, Gliwice, Poland. As a result, detailed band diagrams have been experimentally determined for sol gel films of ZnO [43] and SnO_2 [30]. Results indicate that such films are extremely oxygen deficient. For ZnO, defects must be present which serve as acceptor, donor and trap at the same time [43]. A new method for the detailed analysis of the angle dependence of X-ray photoelectron spectra has been developed for the ex situ characterisation of the electronic structure of thin semiconducting films [30].

The presence of defects in a wide bandgap semiconductor manifests itself in the photoluminescence (PL) spectra. For ZnO (band gap ~3.4 eV), PL is now observed also after excitation below the bandgap, e.g. in the visible. In spherical ZnO micro-resonators, this PL can couple to whispering gallery modes. The shift of such modes in turn can be used to sense the refractive index of the surrounding medium [44]. Absorption of visible light of ZnO micro- and nanostructures is also facilitating photocatalytic reactions, as shown for the decomposition of an organic dye. Interestingly, the ZnO photocatalysts produced for this study have been prepared by cathodic delamination, i.e. a corrosion process [45].

Metal colloids are frequently used as electrocatalysts. A new synthesis strategy for gold particles without organic capping agents from a mixture of water and dimethylformamide has been systematically exploited. By variation of the solvent composition, particles with different morphologies were obtained. At low water content, particles with the catalytically active Au(110) dominate [46].

Measurement and targeted **steering of molecular interaction forces is another fundamental necessity to understanding stability and synthesis of novel functional interfaces and coatings**. In particular, interactions between hydrophobic groups are fundamental in self-assembly and hierarchical structuring of soft matter. The molecular origin of hydrophobic interaction forces is however still not fully revealed, and seems to strongly depend on how water dipoles are arranged around hydrophobes. We recently confirmed experimentally that the hydrophobic force law, which characterizes the interaction of two hydrophobes in aqueous electrolytes, is both long-ranged and exponential down to distances of about 1–2 nm over large concentration regimes from 1 mM to 1 M salt concentrations [47-48]. In addition, we utilized functional carborane self-assembled monolayers to directly tune the molecular dipole moments of water molecules at hydrophobic interfaces. Our data showed that dipoles that are oriented parallel to a hydrophobic surface-plane can induce very long-range interaction forces due to lateral formation of giant dipoles [49]. Hence, surface dipoles may additionally lead to an orientation of water molecules at hydrophobic surfaces.

Another important aspect of functional materials are the swelling/shrinkage dynamics during exposure to different environments. This includes for instance release of molecules from porous media as well as the swelling of organic coatings. For model studies of such swelling dynamics we used Metal-Organic Frameworks (MOFs) which are three dimensional (3D) crystalline coordination polymers consisting of metal ions linked by organic ligands. Gas adsorption in MOFs crystals can dramatically affect their size (expansion and/or shrinkage) or lead to distortion of their porous structure/framework. This behaviour can strongly affect the performance of MOF-based gas storage devices. We showed how white light multiple beam interferometry (MBI) allows to measure in real-time (msec time resolution) the deformations (Å distance resolution) of MOF crystals during cyclic changes between an inert gas (Ar) and humidity. Dynamic and non-monotonic deformation behaviour (contraction/expansion) due to gradual filling of the different adsorption sites present in the unit cell of the crystal was measured for the first time *in-situ* with high time resolution [50]. These studies will now be extended into the measuring of hydrogen loading/ unloading kinetics of various MOF systems as well as to study shrinkage/expansion of e.g. organic coating on corroding metal surfaces.

Industrial processes

In collaboration with different industrial partners, the GO continued to work on fundamentals of the formation of **conversion coatings**. Phosphating is still the most frequently applied pre-treatment process, but requires special attention on new metallic coatings and on modern steels. Electrochemically assisted phosphating is one option to obtain homogeneous phosphate coatings on inhomogeneous substrates, and also on high-strength steels [51-52]. Detailed investigations of aluminum silicon coated steel contribute to the puzzle for understanding the exact role of the titanium phosphate activation bath. Scanning Auger microscopy shows a phosphate distribution after activation that is reverse to the distribution of zinc phosphate crystals after phosphating [53]. Statistical analysis of the size of phosphate crystals after different times of electrochemically triggered phosphating shows that the activation leads to a slower and more homogeneous growth of phosphate during phosphating. Crystals on non-activated surfaces appear to become larger after shorter phosphating times. Overall, there is a strong effect of the activation bath on phosphate growth, but nucleation appears to be less affected [51].

Nanoceramic, e.g. ZrO_2-based conversion coatings are bound to replace phosphating in the future. In collaboration with partners of the chemical industry, the role of Cu^{2+} added to the deposition solution on the formed conversion coatings was investigated. It turns out that the corrosion-promoting Cu^{2+} enhances

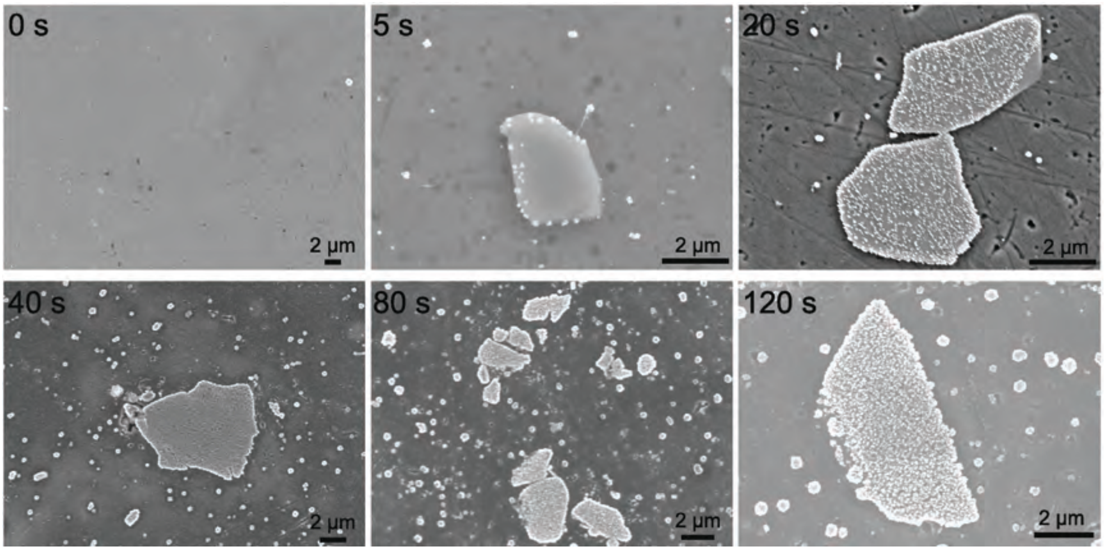


Fig. 4: *SEM images of pretreated AA6014 substrates after different immersion time [54].*

deposition of the conversion coating around intermetallic particles, and at grain boundaries (Fig. 4). This “controlled corrosion process” during conversion coating formation may be crucial in the protection of the inhomogeneous surfaces in “real” materials [54]. Further recent activities include an investigation of the changes in the oxidic conversion layer after electrochemical polarisation.

Joining different materials by welding is an important industrial process, but some material combinations are not accessible in the classic welding processes that involve melting. In collaboration with the Institute of Production Engineering and Forming Machines of TU Darmstadt headed by P. Groche within the DFG-funded priority programme SPP1640 “Joining by forming”, the role of the interface chemistry on cold welding of steels and aluminum alloys is being investigated. Primary heat treatment of the partners critically influences the mechanical properties of the surfaces, and hence affects the bond formation [55]. On the microscopic and nanoscopic level, a thin reaction layer consisting of Fe and Al was found at the interface between steel and aluminum alloy [56], that may be critical for the adhesion, i.e. weld formation. The exact nature of this layer is subject of current investigations. Likewise, the corrosion behaviour of such cold-welded structures is currently being investigated. Attempts to create a simple model experiment that permits studies of well-defined samples to extract essential physicochemical parameters in the cold welding process are a further field of work [57].

Moreover, zinc based metallic coatings are of tremendous importance for corrosion protection and are object of research since decades. Predicting the long term performance of novel zinc alloy coatings is still a problem (see Corrosion above). A new challenge is the so called hot stamping. The development of metal coatings that are suitable for that process and still provide reliable cathodic protection and good long term corrosion performance is the main target of a project financed by the Federal Ministry of Education and Research (KOWUB). The main activity of the MPIE is to investigate the potential of iron rich Fe-Zn-Mg alloys.

The fully automated SFC has been also extended for the analysis of real, high surface-area electrocatalysts, which are important in electrochemical energy conversion devices such as fuel cells and electrolysers. This has been highly beneficial as the wide parameter-space for material composition and structure as well as operation conditions require also fast screening techniques to obtain reliable information within a reasonable timeframe. The SFC has been shown to reliably acquire the activity and the stability of noble metal catalysts with high-throughput [58], and is currently employed for a wide range of different types of porous materials including exciting non-noble catalysts for oxygen reduction [59].

Fundamental problems of oxidation and hydrogen uptake during industrial production steps of high strength steel sheet have been the focus of the Christian Doppler Laboratory of Michael Rohwerder.

Scientific Groups

Electrocatalysis (K. 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.

The new electrochemical methods, which have been developed in the group over the last years [58, 60-61], are utilized to investigate a wide range of scientific challenges. High-throughput combinatorial screening tools combined with sophisticated automation and advanced methods for data evaluation and processing are central for the more systematic and reliable investigation of a large number of samples. In addition, coupling electrochemistry with online reaction product determination by Inductively Coupled Plasma Mass Spectrometry [61] and Differential Electrochemical Mass Spectrometry [62] increases the information depth significantly.

These advanced techniques have provided new exciting insights into processes at the solid-liquid interface particularly of materials for electrochemical energy conversion. The key reactions studied in our laboratory include the oxygen reduction reaction (ORR) and evolution (OER), as well as the utilization of CO_2 by electrochemical means for the production of so-called solar fuels [63]. In contrast to the plain activity evaluation of catalyst materials that dominate the literature in the field, we focus on the overall performance including stability and selectivity, as operation over extended times is crucial for the success of fuel cells and electrolysers. Namely, the conditions during the reactions in these devices are often quite harsh and lead to corrosion of the catalyst material, even though they typically consist of noble metals. Pt, which is among the most active materials for the ORR, for instance dissolves significantly during transient operation when the surface alternates between reduced and oxidized condition [64-66]. Au instead dissolves continuously and to a major extent during steady-state operation at positive potentials close to the oxygen evolution, since it does not form a passivating oxide layer as Pt [67-70]. All noble metals have in common that they dissolve to a certain extent, but clearly there is no inverse relationship between activity and stability as commonly believed [71]. When noble metals are alloyed with transition metals to enhance the intrinsic activity, the dissolution becomes more complex, yet still the performance can be resolved with our special techniques [72-73]. Indeed, only in these investigations of material libraries the full potential of the approach becomes obvious, which will in future also be further extended to the investigation of different catalyst materials like the promising Ru and Ir oxides for the OER [74-75].

Besides these studies on rather model like electrode surfaces, we are also highly interested in real, high surface area catalysts as typically employed in real reactors. The aim is to additionally enhance the fundamental understanding of the structural effects on performance, in order to derive catalyst design principles and achieve optimal operation in applications [76]. In joint efforts with various expert material science groups we therefore contribute to the development of new catalysts, eventually with lower content of scarce noble metals. For instance, together with the department of F. Schüth from the Max-Planck-Institute für Kohlenforschung the concept of “confined space alloying” has been introduced, providing alloy catalysts with unprecedented structural and chemical stability [77-78]. Furthermore, in collaboration with the National Institute for Chemistry in Slovenia, we have demonstrated the beneficial effect of ordered alloy nanoparticle catalysts [79-80], while with the TU Berlin we could show the formation and general instability of nanoporous alloys [81]. Non-noble metal catalysts like the exciting examples of F. Jaouen from the University Montpellier have been recently majorly improved and therefore received enormous attention, however the stability still remains a crucial issue [59, 82]. Exactly therefore, the parallel study and the enhancement of our understanding on activity, selectivity and stability will remain of high importance in electrocatalysis for energy conversion.

Atomistic Modelling (S. Wippermann)

The group was established in February 2013 and is performing *ab initio* theory in the otherwise experimental GO department. The group works in direct collaboration with experiment to gain insights into key processes at solid-solid and solid-liquid interfaces, nanostructures and in the gas phase, which are inaccessible by other means. Employing predictive *ab initio* modelling techniques based on density functional theory and beyond, the group focuses on the general fields of materials for solar and chemical energy conversion and storage. For further details see p. 29.

Interface Spectroscopy (A. Erbe)

The Interface Spectroscopy Group continues to work in two directions, (1) the design of interfaces for spectroscopic investigations and application of spectroscopic techniques to study materials surfaces *in situ* and operando and (2) chemical modification of materials' interfaces to tailor surface properties and to investigate failure mechanisms. Several results within the main focus of the department have already been highlighted in the departmental report.

In the optical development part of the group's work, a new direction involved the use of whispering gallery modes (WGMs) in spherical microresonators from oxide semiconductors as relevant in corrosion. Via defect-related light absorption, photoluminescence can be excited in the visible which couples to the WGMs. Results are emission spectra with narrow lines, observed in ZnO and TiO_2 [44, 83]. It is hoped that using WGMs, highly sensitive optical detection of processes at semiconductor interfaces may become possible. Another major advance was achieved in collaboration with the group of C.F. Chou, Academia Sinica, Taipei, Taiwan. Nanogap electrodes were integrated with Raman spectroscopy, which enabled the trapping and spectroscopic detection of individual protein molecules [84]. A similar approach coupled to electrochemical reactions may enable the understanding of electrochemical processes on the molecular level. Scattering of light is an extremely important phenomenon when considering "real" materials. Continuing a collaboration with R. Sigel, currently at the German University in Cairo, Egypt, ellipsometric dynamic light scattering was developed to extract dynamic information of incoherently scattered light in the presence of strong coherent scattering [85], exploiting the analysis of polarisation of light.

Light is not only used to spectroscopically analyse surfaces, but can also be used for different purposes. In high temperature corrosion, optical heating is frequently used. However, heating efficiency depends on the light absorption. In a comparison between surfaces of different roughness, a model was established which takes into account the scattering from rough surfaces and enables an analysis of the light absorption, hence heating, of metals [86]. Also photocatalysis critically depends on the availability of light. Using a corrosion process, ZnO nanostructures were prepared, in which the combination of the defect-related absorption of visible light with the morphology leads to an almost black material. Thus prepared structures are photocatalytically active [45].

The group's expertise in vibrational spectroscopy of interface dominated materials led to active collaborations with the groups of M. Muhler and W. Schuhmann at the Ruhr University Bochum. We contributed both to understanding and practical analysis of the Raman spectrum of graphene [87], as well as the characterisation of graphene and other sp^2 carbon compounds in complex multicomponent materials [88-91]. New collaborations were also established with groups at the Heinrich Heine University Düsseldorf, in organic chemistry [41] and experimental condensed matter physics [92].

New insight into the chemistry of cathodic delamination processes came from the synthesis of acrylate model polymer thin films with well-defined linkage to the interface. Results show that the delamination is controlled by reaction kinetics, but depends on cross linking and hydrophilicity of the polymers, which all had a thickness in the range of ~30 nm. On the other hand, a covalent linkage to the metal significantly reduces the delamination rate [29]. Consequently, several processes must contribute to the overall delamination rate. A further interesting new aspect of cathodic delamination is the observation of chemical oscillations in the amount of corrosion products and in pH by *in situ* and operando Raman spectroscopy. This observation can be explained with the small reaction volume between polymer and metal during delamination. Because of the consumption of water in the oxygen reduction, the confined region at the polymer/metal interface becomes strongly alkaline. In turn, this stops oxygen reduction, leading to a cyclic behaviour (Fig. 5) [93].

The group contributed actively to the Marie Curie Initial Training Network Somatai by the organisation of training events, participation in organisation of the summer school, and contribution of two chapters to a special volume of tutorials in the series Lecture Notes in Physics.

Christian Doppler Laboratory for Diffusion and Segregation during Production of High Strength Steel Sheet (Michael Rohwerder; until Dec. 2014)

The main focus of this lab, which was successfully concluded in 2014, was on fundamental diffusion and segregation problems encountered during the different production steps of high strength steel sheet. Cooperation partners were e.g. the TU Wien (where the P (Pickling) module was carried out which dealt with pickling after hot rolling). The technical motivation behind this lab was 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 was 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 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 and developing a new simulation tool for describing grain-boundary oxidation on a theoretical level, which, however, was successful only to a certain degree [94]. The reason for this is that the assumption of only diffusion of oxygen and thermodynamics of the oxidation reactions to be considered for a simulation of internal oxidation was not sufficient. In dedicated model experiments, for which a high performing high temperature lab was built up [[95-96]], it was found that for the relatively short reaction times to be considered here, the uptake kinetics at the surface play an important role and that these are determined to a great extent by some alloying elements [27].

In general certain combinations of some of the key alloying elements in high strength steels were found to be responsible for significantly enhanced internal oxidation. This is partly due to their effect on the oxygen uptake kinetics and partly also to the effect of the least noble alloying elements as pioneering oxide former, providing nucleation sites for further oxide growth. Unusual high oversaturation values of alloying elements remaining unoxidized in the matrix were measured [97].

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 hydrogen uptake during the latter, it was found that similar to oxygen uptake at high temperatures, also the hydrogen uptake is affected by some alloying elements and by the oxygen activity (i.e. dew point) [27]. Furthermore, the novel method for hydrogen ultra-sensitive hydrogen detection with high spatial resolution based on Kelvin probe developed in the prior reporting period was applied to a number of materials for characterisation of hydrogen distribution and its role on embrittlement, as well as for hydrogen uptake during corrosion [98-100]. For a full characterisation, however, it is necessary to combine different techniques, including the novel thermo-desorption set up for high sensitive analysis of hydrogen trapping [101] and Time of Flight – Secondary Ion Mass Spectroscopy ToF-SIMS, see also method development Hydrogen Mapping.

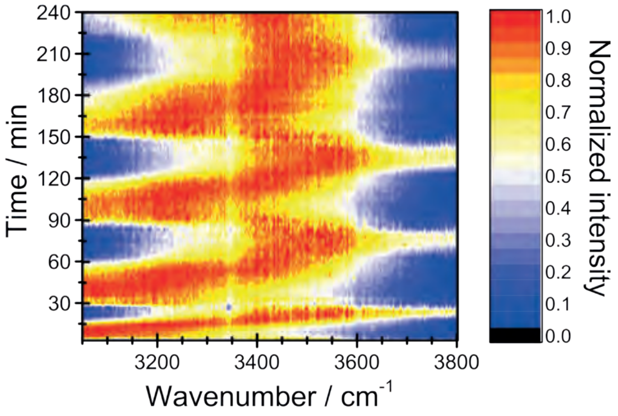


Fig. 5: *Time evolution of false coloured Raman spectra of the OH stretching mode region in the initial phase of cathodic delamination of poly(vinylbutyral) on zinc in the presence of 1M KCl [93].*

Corrosion (Michael Rohwerder)

The main scope of this group is to address fundamental questions of corrosion, surface and coating technology by isolating the crucial problems behind them and designing model experiments and model samples for their systematic investigation. Two major research projects in the group were carried out in the highly competitive framework programme of the Fraunhofer Society (FHG) and Max Planck Society (MPG) collaborative projects. One project ended within the reporting period (“Active Coatings”, see below self-healing coatings) and the other one started in 2014 (“Initial Wear”, see p. 145).

The further main activities on the research interests in the Corrosion group 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 approach 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 [31-33]. However, for an in-depth fundamental investigation of the processes underlying delamination, information about the interfacial reaction kinetics is indispensable, which so far has not been accessible. Currently, a novel method is being developed, which combines hydrogen permeation and Kelvin probe (see p. 38). First results on model samples, including self-assembled monolayer films at the interface, show that this novel method is indeed

able to provide direct information on the oxygen reduction rate at the buried interface.Further, the effect of different pre-treatments on the interface with different coatings and their effect on ion mobility was studied in detail for aluminum [102-103].

2. Electrochemistry in the "dry"
   The novel method for hydrogen detection by Kelvin probe relies on ultra-thin palladium films that are evaporated on the surface of the material to be investigated [98]. Over time the hydrogen entering from the sample underneath into the palladium film accumulates, which makes it possible to measure even extremely low release rates that were not accessible before. However, this only works because the loss of hydrogen from the palladium film is negligible. It is unclear why desorption of hydrogen from the palladium film is so surprisingly low. It is assumed that the ultra-thin water layer remaining at room temperature on the surface even under the dry nitrogen gas atmosphere that is used for the measurements, plays an important role in inhibiting desorption. In order to obtain a better understanding of this (and because this could also help with our understanding of electrochemical reaction at buried interfaces) a novel focus of research within the group is the fundamental investigation of electrochemical double layers and how their structure affects the kinetics of reactions such as oxygen reduction. For this purpose a novel lab environment with a newly acquired Near Ambient Pressure – X-ray Photolectron Spectroscopy NAP-XPS has been built up. The research in this new laboratory is partly closely related to the excellence cluster RESOLV.

3. Measurements of Hydrogen distribution and effect on embrittlement
   The novel SKP and SKPFM based method for hydrogen mapping that was developed with the Christian Doppler Laboratory is now becoming a central tool of research on hydrogen related topics, in close cooperation with other departments (see p. 39).

4. Semiconducting properties of surface oxide films
   An especially important topic are novel Zinc-Aluminum-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, but only under certain environmental conditions [13-16]. The novel Fe-Zn-Mg alloys that are currently being developed for application on steel parts that will undergo hot stamping will have to be investigated in terms of their oxide properties, too.

5. Intelligent self-healing concepts for corrosion protection
   After successful finishing of the MPG-FHG cooperative project on active corrosion protection (ASKORR) the main activities on self-healing are currently carried out within the framework of the DFG SPP "Self-Healing Materials" Within the reporting period we succeeded to synergistically combine capsule loaded zinc coatings with capsule loaded organic coatings for superior intelligent self-healing [39]. Other important results were the development of polyaniline PANI based capsules for intelligent release and their modification for use on zinc and first successful application of intelligent corrosion protection [37-38]. Of special importance is the interfacial stability between conducting polymer and the metal surface [104-105]. Furthermore, a novel strategy for addressing also capsules located deep in the organic coating far away from the metal surface was developed by additionally adding non redox active conducting particles, such as carbon black [106]. The current main activity is to investigate how the coating design has to be modified in order to be able to routinely self-heal defects of macroscopic size, such as 1-2 mm broad scratches, with coatings just a 10-20 microns thick. For this, the propagation of the trigger signal for initiating the release at the onset of corrosion in a defect site has to be very fast and it has to be able to travel deep into the coating. Also release and transport of the active agents from the capsules in the coating to the defect site has to be fast and it is necessary to activate as much of the stored compounds for self-healing as possible. This requires a totally new philosophy for coating design.

6. Novel developments with the Scanning Kelvin Probe
   A technique of central importance for many research projects within the group is the Scanning Kelvin Probe technique. Based on our world leading expertise of this technique also novel application fields are explored. The recent development of spatially resolved high-sensitivity hydrogen detection by Kelvin probe (see Christian Doppler Laboratory and p. 39) has sparked new research on the possibilities to further extent the applicability of the Kelvin probe. In cooperation with Christian Michelsen Research a novel Kelvin probe for outdoor use and for through metal corrosion detection (signal mediated by hydrogen activity at the corroding defect and its permeation through the metal) is currently being developed.

Another development is the use of Kelvin probe for assessing oxygen reduction rates at buried interfaces. Also for the investigation of tunnelling junction in molecular electronics the technique was successfully applied [108], as well as for investigation of lipid layers [109].

Interaction Forces and Functional Materials (M. Valtiner)

The research interest of the Interaction Forces group is focused on the broad areas of adhesion in wet environments, molecular structuring at solid/liquid interfaces, reactivity in confinement and high resolution imaging and detection of corrosive processes. The broader scientific aims are (1) to gain insight into the molecular interactions at equilibrated and dynamically changing reactive interfaces. Also, it is studied (2) how molecular interactions translate into macroscopic interactions (scaling and proportionality laws), and (3) new interferometry-based approaches to study dynamic processes *in-situ* are developed. A particular focus is on how molecular structuring at electrified interfaces influences the mentioned processes. In detail the following scientific topics are of current interest:

1. Molecular scaling and proportionality laws at adhesive interfaces over large length scales
   As already mentioned above a unique experimental framework to test the well-renowned Jarzynski's equality was developed, which relates work performed under non-equilibrium conditions. Based on this we developed a scaling strategy that allows us to predict large-scale properties such as adhesion at electrified interfaces on the basis of single-molecule measurements [36].

2. Fundamentals of peptide materials (Collaboration with UC-Santa Barbara)
   In a **joint project with our collaborator Prof. M.S. Shell from UC Santa Barbara, U.S.A.** state-of-the-art **single molecule atomic force microscopy (SM-AFM) hand-in-hand with advanced molecular simulation** studies were combined to obtain innovative fundamental insights into peptide materials, their self-assembly properties, and their ability to mediate interactions at solid/liquid interfaces. Materials made from peptides are becoming of widespread importance for their tunability, biocompatibility, and sustainability & environmental friendliness. Designer self-assembled peptides form a myriad of nanostructures and have been used as materials for tissue engineering and recovery, drug delivery, biosensing, and inorganic templates and scaffolds. Peptides also offer powerful routes to modify interactions at solid interfaces. They readily tune surface properties (from antibacterial to ultra-hydrophobic moieties), and potentially provide platforms for tissue gluing and environmentally friendly adhesives, based on biomimetic concepts.

   Marine animals such as mussels and barnacles e.g. use an optimized hierarchical structure and a large variety of functional peptides sequences in order to achieve unprecedented adhesion in high salt concentration environments. Here, even on a molecular scale the arrangement of individual bonds massively influences adhesive strength. As anticipated adhesive strength increases with an increasing number of bonds in parallel while an increasing number of bonds in series reduces the strength of an adhesive junction. We recently showed how adhesion forces could be manipulated by the number of interacting bonds in parallel and in series using designer peptides [110]. It was shown how the arrangement of individual bonds in an adhesive junction allows a tuning of adhesive strength even without changing the underlying adhesive bond. Further our unique AFM approach allows us to directly measure interaction free energies of peptides with various surfaces [35]. Based on this experimental data simulation probes can be both tested and finally utilized to provide a full molecular level understanding of interactions of peptides with surfaces in aqueous environments. Finally combination of both AFM single molecule force spectroscopy data and Molecular Dynamics MD-simulations is planned, in order to bridge experiment and theory at the solid/liquid interface.

3. Electrochemistry in confined spaces
   Our unique electrochemical surface forces apparatus allows us to utilize white light interferometry (WLI) to directly visualize corrosion processes in real-time, *in-situ* in confined (i.e. buried) geometries [111]. This is a unique experiment that allows to *in situ* study crevice corrosion with unprecedented resolution in time and space. In a first case study, we investigated in detail how pure **aluminum corrodes in crevice geometries and how vanadate ions can effectively inhibit CC of aluminum** (Fig. 2). We are now continuing into this direction and study how various inhibitors also influence crevice corrosion on real alloy samples. For this we are currently constructing a back-scattering version of the EC-SFA.

4. Electric double layers in static and dynamically changing systems (Collaboration with the cluster of excellence – RESOLV at the Ruhr University Bochum). The molecular structure of the electric double layer is essential in electrochemical and natural processes. In particular, ion and water structuring at charged solid/electrolyte interfaces dominate structure and functionality in many

physiological, geological, and technological systems. In technological concentration ranges above 50-100 mM concentrations electrolyte structuring occurs within the range of molecular dimensions. Yet no qualitative or quantitative model exists for predicting ion structuring at solid/liquid interfaces. In collaboration with the Cluster of Excellence RESOLV (see p. 54), we started to use force probe experiments as workhorse to directly probe structural forces at solid7liquid interfaces. For instance we showed how specific ion adsorption can strongly influence how electric charge is compensated in the electric double layer on model ceramic surfaces [113].

5. Influence of trace molecules on structuring of ionic liquids at electrified and charged interfaces

   Within the last years we utilized **force probe experiments and XPS measurements** to directly measure how water and other impurities alter the interfacial structuring and charging characteristics of RTILs on dielectric surfaces and electrified metal surfaces [113]. On ceramic interfaces water can dissolve surface-bound cations, which leads to high surface charging and strong RTIL layering. In contrast, layering of dry RTIL at weakly charged mica surfaces is weakly structured. At electrified gold electrodes the influence of water is limited to interactions within the RTIL layers, and is not related to a direct electrosorption of water on the polarized electrode. Currently, we are testing the influence of other potentially beneficial additives such as organic long-chained molecules and polymer materials. Generating such detailed insights into molecular interface structures will further guide the targeted development of structures at electrified interfaces.

6. High resolution imaging of active corrosion (Collaboration with Hasselt University)

   Together **with our collaborator F.U. Renner from Hasselt University, Belgium, we recently performed a high-resolution *in-situ* atomic force microscopy study of dealloying of Cu–Au alloy surfaces** [115]. It was found that dealloying patterns, and in particular crack initiation are highly influenced and controlled by the choice of inhibitor molecules, and is also affected by larger scale structural defects such as scratches or polishing defects [115] as well as crystallographic surface orientations.

   In this direction we specifically studied how surface cracks formed during local dealloying of Cu_3Au. Crack induction clearly depends on the crystallographic substrate orientation, which is controlling the number density of cracks on each grain [116]. The highest number density was observed on (110) oriented surfaces and the lowest on (001) and (111) grains.

7. Combining electrochemical force probe experiments with optical spectroscopy.

   The technological focus of the group is the design of novel experiments and experimental setups dedicated to understand interfacial dynamics such as specific and non-specific binding and unbinding events at electrified interfaces. Coupling of laser light into our force probe experiments has been successfully realized and implementation of Raman spectroscopy into the electrochemical Surface Forces Apparatus is the next aim, in close collaboration with the Optical Spectroscopy group of Andreas Erbe.

References

1. Nayak, S.; Biedermann, P.U.; Stratmann, M.; and Erbe, A.: Phys. Chem. Chem. Phys. 15 (2013) 5771.

2. Nayak, S.; Biedermann, P.U.; Stratmann, M.; and Erbe, A.: Electrochim. Acta 106 (2013) 472.

3. Pengel, S.: Anwendung eines Quantenkaskadenlasers in der zeitaufgelösten Laserabsorptionsspektroskopie zur kinetischen Untersuchung der elektrochemischen Sauerstoffreduktion an Germanium., Doctoral thesis, Faculty of Chemistry and Biochemistry, Ruhr University Bochum, 2015.

4. Pengel, S.; Niu, F.; Nayak, S.; Tecklenburg, S.; Chen, Y.-H.; Ebbinghaus, P.; Schulz, R.; Yang, L.; Biedermann, P.U.; Gygi, F.; Schmid, R.; Galli, G.; Wippermann, S.M.; and Erbe, A.: Proc. of the 8th Int. Conf. on Advanced Vibrational Spectroscopy (ICAVS) (2015) 130.

5. Koelsch, P.; Muglali, M.I.; Rohwerder, M.; and Erbe, A.: J. Opt. Soc. Am. B: Opt. Phys. 30 (2013) 219.

6. Baimpos, T.; Shrestha, B.R.; Raman, S.: Langmuir 30 (2014) 4322 .

7. Cheng, H.-W.; Stock, P.; Moeremans, B.; Baimpos, T.; Banquy, X.; Renner, F.U.; and Valtiner, M.: Adv. Mater. Inter. 2 (2015) 1500159.

8. Shrestha, B.R.; Baimpos, T.; Raman, S.; and Valtiner, M.: ACS Nano 8 (2014) 5979 .

9. Tecklenburg, S.: Electrochemical Attenuated Total Reflection Infrared Spectroscopic experiments at Hydrogen terminated Silicon single crystal surfaces, Master Thesis, Faculty of Chemistry and Biochemistry, Ruhr University Bochum, 2015.

10. Rossrucker, L.; Mayrhofer, K.J.J.; Frankel, G.S.; and Birbilis, N.: J. Electrochem. Soc. 161 (2014) C115.

11. Rossrucker, L.; Samaniego, A.; Grote, J.-P.; Mingers, A.M.; Laska, C.A.; Birbilis, N.; Frankel, G.S.; and Mayrhofer, K.J.J.: J. Electrochem. Soc. 162 (2015) C333.

12. Laska, C.A.; Auinger, M.; Biedermann, P.U.; Iqbal, D.; Laska, N.; De Strycker, J.; and Mayrhofer, K.J.J.: Electrochim. Acta 159 (2015) 198.

13. LeBozec, N.; Thierry, D.; Rohwerder, M.; Persson, D.P.; Luckeneder, G.H.; and Luxem, L.: Corros. Sci. 74 (2013) 379.
14. LeBozec, N.; Thierry, D.; Peltola, A.; Luxem, L.; Luckeneder, G.H.; Marchiaro, G.; and Rohwerder, M.: Mater. Corros. - Werkst. Korros. 64 (2013) 969.
15. Krieg, R.; Vimalanandan, A.; and Rohwerder, M.: J. Electrochem. Soc. 161 (2014) C156.
16. Vimalanandan, A.; Bashir, A.; and Rohwerder, M.: Mater. Corros. - Werkst. Korros. 65 (2014) 392.
17. Chen, Y.; Schneider, P.; Liu, B.J.; Borodin, S.; Ren, B.; and Erbe, A.: Electronic structure and morphology of dark oxide on Phys. Chem. Chem. Phys. 15 (2013) 9812.
18. Hans, M.; Erbe, A.; Mathews, S.; Chen, Y.; Solioz, M.; and Mücklich, F.: Langmuir 29 (2013) 16160k.
19. Genchev, G.: Sour gas corrosion – corrosion of steels and other metallic materials in aqueous environments containing H2S, *Submitted* to: Online Reference Database Chemistry, Molecular Sciences and Chemical Engineering, Waltham, MA, USA
20. Genchev, G.; Cox, K.; Tran, T.H.; Sarfraz, A.; Bosch, C.; Spiegel, M.; and Erbe, A.: Corros. Sci. 98 (2015) 725.
21. Enning, D.; Venzlaff, H.; Garrelfs, J.; Dinh, H. T.; Meyer, V.; Mayrhofer, K.; Hassel, A. W.; Stratmann, M.; Widdel, F.; Environ Microbiol 14 (2012) 1772.
22. Beese-Vasbender, P.F.; Venzlaff, H.; Srinivasan, J.; Garrelfs, J.; Stratmann, M.; and Mayrhofer, K.J.J.: Electrochim. Acta 105 (2013) 239.
23. Venzlaff, H.; Enning, D.; Srinivasan, J.; Mayrhofer, K.J.J.; Hassel, A.W.; Widdel, F.; and Stratmann, M.: Corros. Sci. 66 (2013) 88.
24. Beese-Vasbender, P.F.; Nayak, S.; Erbe, A.; Stratmann, M.; and Mayrhofer, K.J.J.: Electrochim. Acta 167 (2015) 321.
25. Beese-Vasbender, P.F.; Grote, J.-P.; Garrelfs, J.; Stratmann, M.; and Mayrhofer, K.J.J.: Bioelectrochem. 102 (2015) 50.
26. Shrestha, B.R.; Hu, Q.; Baimpos, T.; Kristiansen, K.; Israelachvili, J.N.; and Valtiner, M.: J. Electrochem. Soc. 162 (2015) C327.
27. Borodin, S.; Vogel, D.; Swaminathan, S.; and Rohwerder, M.: Oxid. Met. (2015)
28. Iqbal, D.; Moirangthem, R.S.; Bashir, A.; and Erbe, A.: Mater. Corros. - Werkst. Korros. 65 (2014) 370.
29. Iqbal, D.; Rechmann, J.; Sarfraz, A.; Altin, A.; Genchev, G.; and Erbe, A.: ACS Appl. Mater. Inter. 6 (2014) 18112.
30. Krzywiecki, M.; Sarfraz, A.;Erbe, A.: Applied Physics Letters *submitted*.
31. Bashir, A.; Azzam, W.; Rohwerder, M.; and Terfort, A.: Langmuir 29 (2013) 13449.
32. Bashir, A.; Heck, A.; Narita, A.; Feng, X.; Nefedov, A.; Rohwerder, M.; Muellen, K.; Elstner, M.; and Wöll, C.H.: Phys. Chem. Chem. Phys. 17 (2015) 21988.
33. Muglali, M.I.; Erbe, A.; Chen, Y.; Barth, C.; Koelsch, P.; and Rohwerder, M.: Electrochim. Acta 90 (2013) 17.
34. Kemnade, N.; Chen, Y.; Muglali, M.I.; and Erbe, A.: Phys. Chem. Chem. Phys. 16 (2014) 17081.
35. Raman, S.; Utzig, T.; Baimpos, T.; Shrestha, B.R.; and Valtiner, M.: Nat. Commun. 5 (2014) 5539.
36. Utzig, T.; Raman, S.; and Valtiner, M.: Langmuir 31 (2015) 2722
37. Lv, L.-P.; Zhao, Y.; Vilbrandt, N.; Gallei, M.; Vimalanandan, A.; Rohwerder, M.; Landfester, K.; and Crespy, D.: J. Am. Chem. Soc.135 (2013) 14198.
38. Vimalanandan, A.; Lv, L.-P.; Tran, T.H.; Landfester, K.; Crespy, D.; and Rohwerder, M.: Adv. Mater. 25 (2013) 6980.
39. Tran, T.H.; Vimalanandan, A.; Genchev, G.; Fickert, J.; Landfester, K.; Crespy, D.; and Rohwerder, M.: Adv. Mater. 27 (2015) 3825.
40. Stock, P.; Erbe, A.; Buck, M.; Wiedemann, D.; Ménard, H.; Hörner, G.; and Grohmann, A.: Z. Naturforsch. B 69b (2014) 1164.
41. Rechmann, J.; Sarfraz, A.; Götzinger, A.C.; Dirksen, E.; Müller, T.J.J.; and Erbe, A.: Langmuir 31 (2015) 7306.
42. Pang, B.: Synthesis of photosensitive molecules and characterization of their adsorbates on Au(111) Surface, Master Thesis, Faculty of Chemistry and Biochemistry, Ruhr University Bochum, 2014
43. Krzywiecki, M.; Grządziel, L.; Sarfraz, A.; Iqbal, D.; Szwajca, A.; and Erbe, A.: Phys. Chem. Chem. Phys. 17 (2015) 10004.
44. Moirangthem, R.S.; and Erbe, A.: Appl. Phys. Lett. 103 (2013) 051108.
45. Iqbal, D.; Kostka, A.; Bashir, A.; Sarfraz, A.; Chen, Y.; Wieck, A.D.; and Erbe, A.: ACS Appl. Mater. Inter. 6 (2014) 18728.
46. Chen, Y.; Fernandes, A.A.; and Erbe, A.: Electrochim. Acta 113 (2013) 810.
47. Stock, P.; Utzig, T.; and Valtiner, M.: J. Colloid Interf. Sci. 446 (2015) 244.
48. Donaldson Jr., S.H.; Røyne, A.; Kristiansen, K.; Rapp, M.V.; Das, S.K.; Gebbie, M.A.; Lee, D.; Stock, P.; Valtiner, M.; and Israelachvili, J.N.: Langmuir 31 (2015) 2051.
49. Kristiansen, K.; Stock, P.; Baimpos, T.; Raman, S.; Harada, J.K.; Israelachvili, J.N.; and Valtiner, M.: ACS Nano 8 (2014) 10870.
50. Baimpos, T.; Shrestha, B.R.; Hu, Q.; Genchev, G.; and Valtiner, M.: J. Phys. Chem. C 119 (2015) 16769.
51. Erbe, A.; Schneider, P.; Gadiyar, C.; Renner, F. U.;Electrochimica Acta *submitted*.

52. Schneider, P.: Studie über die Anfangsstadien und die Aktivierungsprozesse der Phosphatierung auf aluminium- und siliziumhaltigen Oberflächen, Doctoral thesis, Faculty of Physics and Astronomy, Ruhr University Bochum, 2013
53. Schneider, P.; Sigel, R.; Lange, M.M.; Beier, F.; Renner, F.U.; and Erbe, A.: ACS Appl. Mater. Inter. 5 (2013) 4224.
54. Sarfraz, A.; Posner, R.; Lange, M.M.; Lill, K.A.; and Erbe, A.: J. Electrochem. Soc. 161 (2014) C509.
55. Groche, P.; Wohletz, S.; Erbe, A.; and Altin, A.: J. Mater. Process. Technol. 214 (2014) 2040
56. S. W. A. Altin, W. Krieger, A. Kostka, P. Groche, A. Erbe, Advanced Materials Research 2014, 966-967, 445-452
57. Krieger, W.: Fügen von Stahl und Aluminium bei Raumtemperatur Master thesis, Faculty of Mechanical Engineering, Ruhr University Bochum, 2014
58. Schuppert, A. K.; Topalov, A. A.; Katsounaros, I.; Klemm, S. O.; Mayrhofer, K. J. J.: Journal of the Electrochemical Society 159 (2012) F670.
59. Choi, C. H.; Baldizzone, C.; Grote, J.-P.; Schuppert, A. K.; Jaouen, F.; Mayrhofer, K. J. J.: Angewandte Chemie International Edition 2015 *submitted*.
60. Topalov, A. A.; Katsounaros, I.; Meier, J. C.; Klemm, S. O.; Mayrhofer, K. J. J.: Review of Scientific Instruments 82 (2011) 114103.
61. Klemm, S. O.; Topalov, A. A.; Laska, C. A.; Mayrhofer, K. J. J.: Electrochemistry Communications 13 (2011) 1533.
62. Grote, J.-P.; Žeradjanin, A.R.; Cherevko, S.; and Mayrhofer, K.J.J.: Rev. Sci. Instrum. 85 (2014) 104101.
63. Katsounaros, I.; Cherevko, S.; Žeradjanin, A.R.; and Mayrhofer, K.J.J.: Angew. Chem. Int. Ed. 53 (2014) 102.
64. Topalov, A.A.; Katsounaros, I.; Auinger, M.; Cherevko, S.; Meier, J.C.; Klemm, S.O.; Mayrhofer, K.J.J.: Angew Chem Int Edit 51 (2012) 12613.
65. Topalov, A.A.; Cherevko, S.; Žeradjanin, A.R.; Meier, J.C.; Katsounaros, I.; and Mayrhofer, K.J.J.: Chem. Sci. 5 (2013) 631.
66. Cherevko, S.; Topalov, A.A.; Žeradjanin, A.R.; Keeley, G.P.; and Mayrhofer, K.J.J.: Electrocatalysis 5 (2014) 235.
67. Cherevko, S.; Topalov, A.A.; Katsounaros, I.; and Mayrhofer, K.J.J.: Electrochem. Commun. 28 (2013) 44.
68. Cherevko, S.; Topalov, A.A.; Žeradjanin, A.R.; Katsounaros, I.; and Mayrhofer, K.J.J.: RSC Adv. 3 (2013) 16516.
69. Cherevko, S.; Žeradjanin, A.R.; Keeley, G.P.; and Mayrhofer, K.J.J.: J. Electrochem. Soc. 161 (2014) H822.
70. Cherevko, S.; Žeradjanin, A.R.; Topalov, A.A.; Keeley, G.P.; and Mayrhofer, K.J.J.: J. Electrochem. Soc. 161 (2014) H501.
71. Cherevko, S.; Žeradjanin, A.R.; Topalov, A.A.; Kulyk, N.; Katsounaros, I.; and Mayrhofer, K.J.J.: ChemCatChem 6 (2014) 2219.
72. Schuppert, A.K.; Topalov, A.A.; Savan, A.; Ludwig, A.; and Mayrhofer, K.J.J.: ChemElectroChem 1 (2014) 358.
73. Schuppert, A.K.; Savan, A.; Ludwig, A.; and Mayrhofer, K.J.J.: Electrochim. Acta 144 (2014) 332.
74. Žeradjanin, A.R.; Topalov, A.A.; Van Overmeere, Q.; Cherevko, S.; Chen, X.; Ventosa, E.A.; Schuhmann, W.; and Mayrhofer, K.J.J.: RSC Adv. 4 (2014) 9579.
75. Cherevko, S.; Reier, T.; Žeradjanin, A.R.; Pawolek, Z.; Strasser, P.; and Mayrhofer, K.J.J.: Electrochem. Commun. 48 (2014) 81.
76. Meier, J.C.; Galeano Nuñez, D.C.; Katsounaros, I.; Witte, J.; Bongard, H.-J.; Topalov, A.A.; Baldizzone, C.; Mezzavilla, S.; Schüth, F.; and Mayrhofer, K.J.J.: Beilstein J. Nanotechnol. 5 (2014) 44 .
77. Baldizzone, C.; Mezzavilla, S.; Carvalho, H.W.P.; Meier, J.C.; Schuppert, A.K.; Heggen, M.; Galeano Nuñez, D.C.; Grunwaldt, J.-D.; Schüth, F.; and Mayrhofer, K.J.J.: Angew. Chem. Int. Ed. 53 (2014) 14250.
78. Baldizzone, C.; Mezzavilla, S.; Hodnik, N.; Žeradjanin, A.R.; Kostka, A.; Schüth, F.; and Mayrhofer, K.J.J.: Chem. Commun. 51 (2015) 1226.
79. Jeyabharathi, C.; Hodnik, N.; Baldizzone, C.; Meier, J.C.; Heggen, M.; Phani, K.L.; Bele, M.; Zorko, M.; Hočevar, S.; and Mayrhofer, K.J.J.: ChemCatChem 5 (2013) 2627.
80. Hodnik, N.; Jeyabharathi, C.; Meier, J.C.; Kostka, A.; Phani, K.L.; Rečnik, A.; Bele, M.; Hočevar, S.; Gaberšček, M.; and Mayrhofer, K.J.J.: Phys. Chem. Chem. Phys. 16 (2014) 13610.
81. Baldizzone, C.; Gan, L.; Hodnik, N.; Keeley, G.P.; Kostka, A.; Heggen, M.; Strasser, P.; and Mayrhofer, K.J.J.: ACS Catal. 5 (2015) 5000.
82. Goellner, V.; Baldizzone, C.; Schuppert, A.K.; Sougrati, M.T.; Mayrhofer, K.J.J.; and Jaouen, F.: Phys. Chem. Chem. Phys. 16 (2014) 18454.
83. Paunoiu, A.; Moirangthem, R.S.; and Erbe, A.: Phys. Status Solidi (RRL) 9 (2015) 241.
84. Lesser-Rojas, L.; Ebbinghaus, P.; Vasan, G.; Chu, M.-L.; Erbe, A.; and Chou, C.-F.: Nano Lett. 14 (2014) 2242.
85. Erbe, A.; and Sigel, R.: Phys. Chem. Chem. Phys. 15 (2013) 19143.
86. Auinger, M.; Ebbinghaus, P.; Blümich, A.; and Erbe, A.: J. Eur. Opt. Soc. Rapid 9 (2014) 14004.
87. Sun, Z.; Dong, N.; Xie, K.; Xia, W.; König, D.; Nagaiah, T.C.; Sánchez, M.D.; Ebbinghaus, P.; Erbe, A.; Ludwig, A.; Schuhmann, W.; Wang, J.; and Muhler, M.: J. Phys. Chem. C 117 (2013) 11811.

88. Sun, Z.; Pöller, S.; Huang, X.; Taetz, C.; Ebbinghaus, P.; Masa, J.; Erbe, A.; Kilzer, A.; Schuhmann, W.; and Muhler, M.: Carbon 64 (2013) 288.

89. Sun, Z.; Xie, K.; Li, Z.A.; Sinev, I.; Ebbinghaus, P.; Erbe, A.; Farle, M.; Schuhmann, W.; Muhler, M.; and Ventosa, E.: Chem. - Eur. J. 20 (2014) 2022.

90. Sun, Z.; Vivekananthan, J.; Guschin, D.A.; Huang, X.; Kuznetsov, V.L.; Ebbinghaus, P.; Sarfraz, A.; Muhler, M.; and Schuhmann, W.: Chem. - Eur. J. 20 (2014) 5752.

91. Xie, K.; Yang, F.; Ebbinghaus, P.; Erbe, A.; Muhler, M.; Xia, W.: J. Energy Chem. 24 (2015) 407.

92. El Achhab, M.; Erbe, A.; Koschek, G.; Hamouich, R.; and Schierbaum, K.: Appl. Phys. A 116 (2014) 2039.

93. Iqbal, D.; Sarfraz, A.; Stratmann, M.; and Erbe, A.: Chem. Commun. 51 (2015) 16041.

94. Auinger, M.; Vogel, A.; Vogel, D.; and Rohwerder, M.: Corros. Sci. 86 (2014) 183.

95. Auinger, M.; Vogel, D.; Vogel, A.; Spiegel, M.; and Rohwerder, M.: Rev. Sci. Instrum. 84 (2013) 085108.

96. Auinger, M.; Vogel, A.; Praig, V.G.; Danninger, H.; and Rohwerder, M.: TCorros. Sci. 78 (2014) 188.

97. Wengert, A.: Master thesis, Faculty of Mechanical Engineering, Ruhr University Bochum, 2015

98. Evers, S.; Senöz, C.; and Rohwerder, M.: Sci. Technol. Adv. Mater. 14 (2013) 014201.

99. Evers, S.; Senöz, C.; and Rohwerder, M.: Electrochim. Acta 110 (2013) 534.

100. Koyama, M.; Bashir, A.; Rohwerder, M.; Merzlikin, S.V.; Akiyama, E.; Tsuzaki, K.; and Raabe, D.: J. Electrochem. Soc. 162 (2015) C638.

101. Merzlikin, S.V.; Borodin, S.; Vogel, D.; and Rohwerder, M.: Talanta 136 (2015) 108.

102. Salgin, B.; Özkanat, Ö.; Mol, J.M.C.; Terryn, H.A.; and Rohwerder, M.: The J. Phys. Chem. C 117 (2013) 4480.

103. Salgin, B.; Hamou, F.R.; and Rohwerder, M.: Electrochim. Acta 110 (2013) 526.

104. Luo, Y.; Vimalanandan, A.; Wang, X.; and Rohwerder, M.: Electrochim. Acta 161 (2015) 10.

105. Luo, Y.; Wang, X.; Guo, W.; and Rohwerder, M.: J. Electrochem. Soc. 162 (2015) C294.

106. Bai, X.; Tran, T.H.; Yu, D.; Vimalanandan, A.; Hu, X.; and Rohwerder, M.: Corros. Sci. 95 (2015) 110.

107. Bai, X.; Hu, X.; Zhou, S.; Li, L.; and Rohwerder, M.: Compos. Sci. Technol. 110 (2015) 166.

108. Fracasso, D.; Muglali, M.I.; Rohwerder, M.; Terfort, A.; and Chiechi, R.C.: J. Phys. Chem. C 117 (2013) 11367.

109. Ghosh, S.K.; Salgin, B.; Pontoni, D.; Reusch, T.C.G.; Keil, P.; Vogel, D.; Rohwerder, M.; Reichert, H.G.; and Salditt, T.: Langmuir 29 (2013) 815.

110. Utzig, T.; Stock, P.; Raman, S.; Valtiner, M.; Langmuir 2015, *submitted*.

111. Shrestha, B.R.; Hu, Q.; Baimpos, T.; Kristiansen, K.; Israelachvili, J.N.; and Valtiner, M.: J. Electrochem. Soc. 162 (2015) C327.

112. Baimpos, T.; Shrestha, B.R.; Raman, S.; and Valtiner, M.: Langmuir 30 (2014) 4322.

113. Cheng, H.-W.; Stock, P.; Moeremans, B.; Baimpos, T.; Banquy, X.; Renner, F.U.; and Valtiner, M.: Adv. Mater. Inter. 2 (2015) 1500159.

114. Valtiner, M.; Ankah, G. N.; Bashir, A.; Renner, F. U.: Review of Scientific Instruments 82 (2011) 023703.

115. Shrestha, B. R.; Bashir, A.; Valtiner, M.; Renner, F. U.; Faraday Discussion - Corrosion 2015, *accepted*.

116. Renner, F.U.; Ankah, G.N.; Bashir, A.; Ma, D.; Biedermann, P.U.; Shrestha, B.R.; Nellessen, M.; Khorashadizadeh, A.; Losada-Pérez, P.; Duarte, M.J.; Raabe, D.; and Valtiner, M.: Adv. Mater. 27 (2015) 4877.

Research Projects in Progress

Electrocatalysis

Baldizzone: Degradation of carbon-supported Pt bimetallic nanoparticles

Cherevko, Zeradjanin, Grote: High-throughput material screening for electrochemical CO_2 reduction

Grote, Zeradjanin, Cherevko: CO_2 reduction product analysis by SFC coupled with DEMS

Cherevko, Kasian: Mechanism of metal oxide dissolution in acidic media

Geiger: Investigation of high-surface area catalysts for OER

Kasian, Cherevko, Geiger, Ludwig: Investigation of material libraries based on nobel metal oxides

Zeradjanin: Key denominators for HER/HOR

Kulyk: Modelling of mass transport and cell geometry impacts on electrochemical reactions

Keeley: Particle-size effects on dissolution of noble metals

Hodnik: Development of electrochemical *in-situ* electron microscopy

Pizzutilo: Oxygen reduction reaction on noble metal catalysts

Pizzutilo: Hydrogen peroxide production on AuPd alloys

Polymeros, Baldizzone: Study of fuel cell catalyst stability under simulated start up/ shut down conditions

Polymeros: Development of an advanced characterization tool for high-surface area catalysts

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

Baldizzone, Pizzutilo, Schüth: Influence of catalyst support on activity and stability - hollow graphitic sphere based platinum nanoparticles

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

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

Choi: Single atom catalysts for electrochemical reactions

Choi, Grote: Stability of non-noble catalysts for ORR

Interface Spectroscopy

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

Altin, Krieger, Wohletz, Groche, Springer, Erbe: Corrosion of aluminium-steel joints prepared by cold forging

Chen, Erbe: Step-scan FTIR studies of electrode/electrolyte interfaces

Chen, Toparli, Erbe: Characterisation of organic corrosion inhibitors on copper

Ebbinghaus, Erbe: Visualisation of delamination by infrared microscopy

Fernandez Solis, Rohwerder, Erbe: Coatings based on water-soluble biopolymers

Genchev, Todorova, Springer, Erbe: Corrosion of iron-based alloys in H_2S-containing media

Ksiazkiewicz, Fernandez Solis, Erbe: Characterisation of oxidation products of biopolymer films on zinc

Mondragon Ochoa, Rohwerder, Erbe: Synthesis and electrochemical characterisation of well-defined thin model polymers by atomic transfer radical polymerisation

Niu, Schulz, Schmid, Erbe: Analysis of electrode potential dependent water structure at the germanium/electrolyte interface by attenuated total reflection infrared spectroscopy

Pander, Tecklenburg, Yang, Wippermann, Erbe: Stabilisation of the silicon/electrolyte interface for infrared spectroscopic investigations

Rabe, Erbe: Mechanistic investigations of the oxygen evolution reaction on manganese electrodes

Rechmann, Götzinger, Dirksen, Müller, Erbe: Electrochemical properties of phenothiazine-modified metal surfaces

Sarfraz, Toparli, Zeredjanin, Erbe: Investigation of oxide growth at the platinum/electrolyte interface

Schwenzfeier, Hu, Valtiner, Erbe: Development of a matrix method based analysis scheme for interferometric spectra recorded in the surface force aperatus

Tecklenburg, O'Donoghue, Devi, Erbe: Preparation of atomically defined ZnO films and spectroscopic characterisation of its interaction with water

Toparli, Sarfraz, Erbe: Investigation of electrode surfaces in the transpassive regime by *in situ* spectroscopies

Corrosion

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

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

Merzlikin, Rohwerder: TDS characterisation of hydrogen in steels

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

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

Bashir, Rohwerder: SKPFM for the investigation of hydrogen in metals: further developing the technique

Merzlikin, Rohwerder: Novel corrosion protection coatings for hot forming

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

NN, Rohwerder: Role of microstructure in zinc alloy coatings on corrosion performance

Evers, Rohwerder: Investigation of the potential use of Kelvin Probe for detection of corrosion at the inside of tank and pipeline walls

Evers, Rohwerder: Investigation of the potential use of Kelvin Probe for detection of corrosion under extreme conditions

Merz, Rohwerder: Investigation of optimal distribution of conducting polymer within an organic coating and at the interface with the metal for achieving optimal corrosion protection

Uebel, Rohwerder: Fundamental investigation of coating requirements for fast self-healing of large defect sites in organic coatings

Krieger, Merzlikin, Rohwerder: Role of hydrogen activity on trapping at internal oxides

Krieger, Merzlikin, Springer, Rohwerder: Fundamental investigation of role of microstructure on hydrogen embrittlement

Dandapani, Rohwerder: Investigation of oxygen reduction at the interface between metal and organic coating by use of a novel permeation based technique

Kerger, Rohwerder: In-situ investigation of electrochemical oxygen reduction and metal oxidation by ambient ESCA

Beibei Peng: Fundamental investigation of the emersed electrochemical double layer

Wengert, Vogel, Vogel, Rohwerder: investigation of oxygen uptake and its effect on short term internal oxidation

Wu, NN, Rohwerder: Characterization of hydrogen trapping sites in steels at high spatial resolution by means of SKPFM and permeation techniques

Interaction Forces and Functional Materials

Utzig, Stock, Raman, Valtiner: Fundamentals of Peptide Materials

Cheng, Hu, Merola, Baimpos, Valtiner: Electric double layer structures in highly concentrated electrolytes and ionic liquids

Hu, Shrestha, Valtiner: Electrolyte structuring and electric double layers at static and dynamic electrified interfaces

Merola, Hu, Cheng, Shrestha: Corrosion in confinement (Crevice corrosion and stress corrosion cracking)

Merola, Valtiner: Conductivity in ultra-thin surface films (oxides and organic barrier layers).

Buvaneswaran, Gonzalez, Valtiner: Scientific programming of machine controls and feedback mechanism for force spectroscopy and surface forces apparatus.

Buvaneswaran, Valtiner: Design of novel force probe techniques for measuring equilibrated single molecule force distance spectra

Schwenzfeier, Hu, Valtiner, Erbe: Development of a matrix method based analysis scheme for interferometric spectra recorded in the surface force aperatus

Hu, Valtiner: Hydration lubrication, friction and damage in tribological and tribocorroding systems in aqueous solutions.

Cheng, Valtiner: Wetting of nano-confined spaces by battery electrolytes

Baimpos, Valtiner: High-resolution *in-situ* study of the swelling/shrinkage of Metal-Organic-Frameworks during loading/unloading with gas molecules

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

Stock, Utzig, Valtiner: Hydrophobic interactions at the macroscopic and single molecular scale

Stock, Müller, Valtiner: Influence of specifically adsorbing ions on hydrophobic interactions

Raman, Stock, Utzig, Moreno-Ostertag, Valtiner: Single molecule physics at electrified interfaces

Chen, Valtiner: Preparation and manufacturing of dielectric mirrors for interferometry applications

Atomistic Modelling

Scalise, Wippermann: Nanointerfaces in InAs-Sn_2S_6 nanocrystal-ligand networks

Nugraha, Wippermann: 3C-SiC/SiO_2 interfaces in SiC nanofiber-based solar cells: characterization from joint *ab initio* thermodynamics and electron paramagnetic resonance simulations

Yang, Tecklenburg, Wippermann, Erbe: Joint first principles and ATR-IR study of the vibrational properties of interfacial water at Si:H-H_2O solid-liquid interfaces

Kenmoe, Biedermann, Wippermann, Todorova, Neugebauer: Stability and vibrational properties of water thin films on low index ZnO surfaces

Vatti, Yang, Wippermann, Todorova, Neugebauer: Ion solvation energies and solvation shell vibrational dynamics

Biedermann, Todorova, Neugebauer, Wippermann: Surface phase stability at Ge-water interfaces from *ab initio* molecular dynamics

Wippermann: First Principles Kelvin probe force microscopy study of stepped Silicon surfaces

Wippermann: Electron-phonon coupling and impurity mediated charge density wave formation in an atomic layer electronic crystal

Wippermann: Non-thermal metal insulator transition in In/Si(111) nanowires

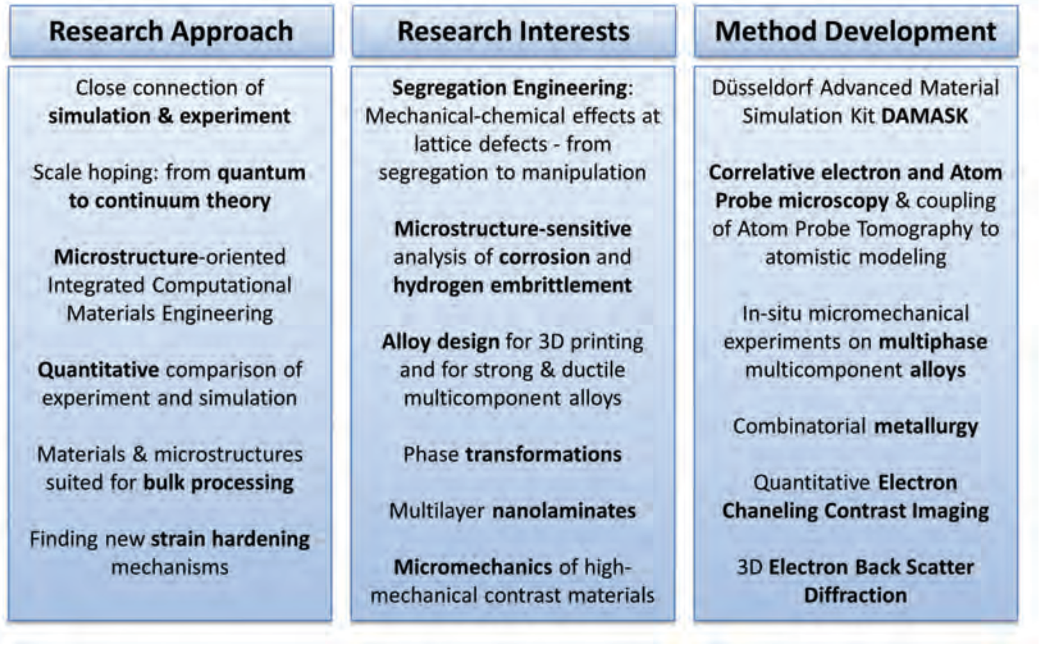
Wippermann: Surface vibrational Raman modes of atomic-scale one-dimensional metallic nanowires

Department of Microstructure Physics and Alloy Design

D. Raabe

Scientific Concept

The department conducts basic research on the relationship between **synthesis, processing, microstructure and properties** of compositionally and structurally **complex materials**. Emphasis lies on nanostructured alloys based on iron, magnesium, titanium, nickel, intermetallics and metal-matrix composites which are characterized by a large variety of **phase transformations**, **kinetics** and **defect substructures**. We apply **advanced characterization** methods from the single atom level up to the macroscopic scale together with **multiscale simulation** methods, focusing on mechanical structure-property relations. Our preferred experimental tools are local electrode atom probe tomography (APT) correlated with transmission electron microscopy (TEM) [1-20], cross-correlation EBSD (electron backscatter diffraction) and 3D EBSD methods [21-24], electron chaneling contrast imaging (ECCI) under controlled diffraction conditions [25-34], and *in-situ* micromechanical experiments correlated to local strain mapping and micromechanical simulations [35-41]. Our modeling tools have been rendered into the modular **freeware simulation package DAMASK** (Düsseldorf Advanced Material Simulation Kit) which is a hierarchically structured model of material point behaviour for the solution of elastoplastic boundary value problems along with damage and thermal effects [42-54]. Our approaches and main topics are shown in Fig. 1. Some of the most exiting scientific fields currently pursued are shown in Fig. 2.



Research Approach	Research Interests	Method Development
Close connection of **simulation & experiment**	**Segregation Engineering**: Mechanical-chemical effects at lattice defects - from segregation to manipulation	Düsseldorf Advanced Material Simulation Kit **DAMASK**
Scale hoping: from **quantum to continuum theory**	**Microstructure-sensitive** analysis of **corrosion** and **hydrogen embrittlement**	**Correlative electron and Atom Probe microscopy** & coupling of Atom Probe Tomography to atomistic modeling
Microstructure-oriented Integrated Computational Materials Engineering	**Alloy design** for 3D printing and for strong & ductile multicomponent alloys	In-situ micromechanical experiments on **multiphase** multicomponent **alloys**
Quantitative comparison of experiment and simulation	Phase **transformations**	Combinatorial **metallurgy**
Materials & microstructures suited for **bulk processing**	Multilayer **nanolaminates**	Quantitative **Electron Chaneling Contrast Imaging**
Finding new **strain hardening** mechanisms	**Micromechanics** of high-mechanical contrast materials	**3D Electron Back Scatter Diffraction**

Fig. 1: *Research approach, interests and corresponding long-term method development in the Department for Microstructure Physics and Alloy Design.*

Research Groups

The department is organized in scientific groups some of which are extramurally funded and hence non-permanent, Fig. 3.

The group '**Theory and Simulation**' of Franz Roters develops mechanism-based constitutive models [55-57] for steels, Ti and Mg alloys, focusing on crystal plasticity approaches [29,35,36,42-54]. Models range from phenomenological descriptions to physics-based formulations of **dislocation** slip, **twin-**

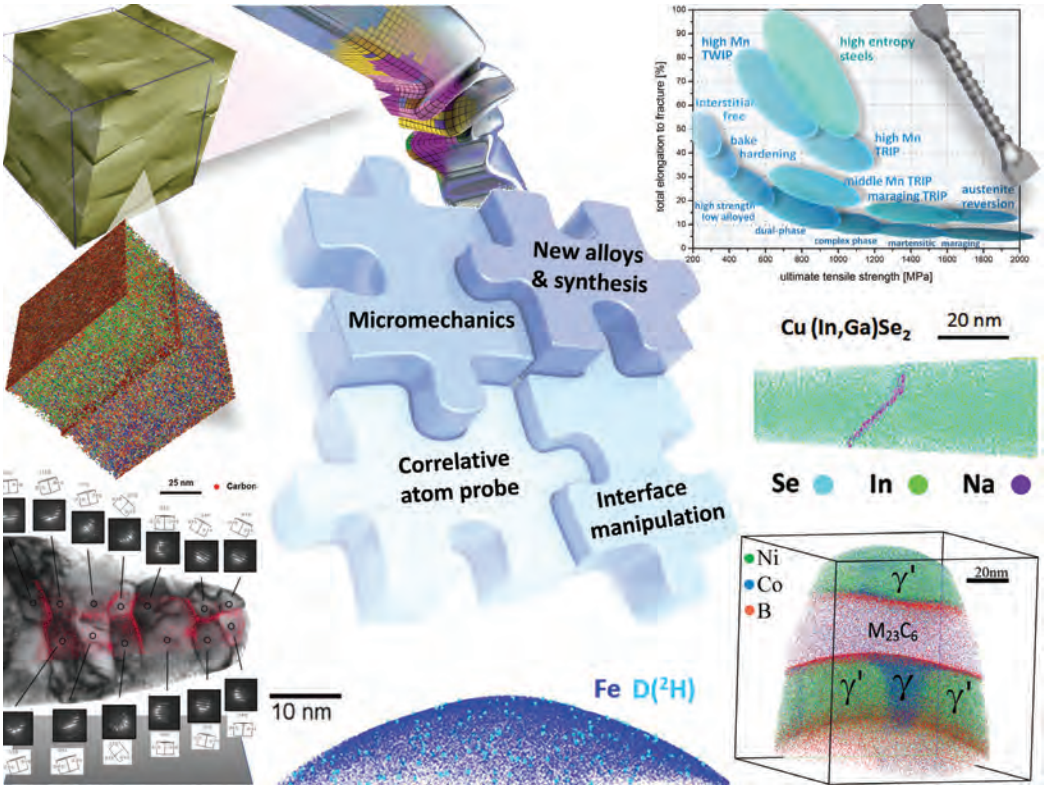


Fig. 2: *Some scientific fields currently pursued in the Department for Microstructure Physics and Alloy Design.*

ning induced plasticity (TWIP) and **martensitic transformations** (TRIP) [29]. The mean field models describe the evolution of lattice defects such as dislocations and twins under given mechanical or thermal boundary conditions. The predicted defect densities enter into kinetic structure-property relations that translate them into strength and deformation measures [55-57]. Owing to the crystalline anisotropy of metallic alloys the constitutive laws assume a tensorial form, i.e. they predict the defect evolutions on all crystallographic shear and twinning systems and their interactions. The resulting sets of nonlinear internal-variable differential equations are solved using either the **Finite Element Method** (CPFEM) or a **Spectral Method** (CPFFT) [58-60]. The models are accessible through the modular simulation framework DAMASK (*http://damask.mpie.de*) [42] (see p. 45).

The group '**Microscopy and Diffraction**' of Stefan Zaefferer pursues two correlated tasks: on the one hand, its projects aim at understanding microstructure formation mechanisms and the relation between microstructures and properties of materials by investigations at the microscopic level. To this aim, several SEM-based microscopy and **electron diffraction techniques** (EBSD, 3D EBSD, XR (cross-correlation)-EBSD, ECCI) have been developed and advanced [21-35]. Imaging and diffraction in transmission electron microscopy (TEM) and x-ray diffraction is conducted as well. With respect to microstructures the focus is on deformation, recrystallization and phase transformations. Concerning properties, corrosion, mechanical behaviour and electronic properties are studied. The spectrum of materials comprises DP (dual phase) steels, TRIP steels, complex phase steels, quench and partitioning steels, electrical steels, austenitic steels, superalloys, Mg-, Al- and Cu alloys, intermetallic compounds and photovoltaic materials [61-64]. The group operates several instruments, e.g. a Zeiss Crossbeam XB1560 FIB-SEM for **3D EBSD** investigations, a JEOL JSM 6500 F SEM, and a JEOL JSM 840A SEM. These instruments are equipped with EBSD, *in-situ* deformation and heating tools. For TEM a Phillips CM 20 is used. This instrument is equipped with the software **TOCA** for on-line crystallographic analysis. Furthermore, several XRD (x-ray diffraction) goniometers are operated.

The group '**Alloy Design and Thermomechanical Processing**' of Dirk Ponge works on the microstructure-oriented **design of advanced high strength steels** and Ni- and Ti-alloys [65-72]. Projects focus on strain hardening mechanisms in complex engineering alloys, making use of processing, mechanical testing and microstructure characterization down to the atomic scale [1,2,73,74]. Thermomechanical processing is a main objective in optimizing steel microstructures and mechanical properties. Main examples are the design of ultrafine grained C-Mn steels and **dual phase (DP)**

Research Groups

- **Theory & Simulation**
- **Microscopy & Diffraction**
- **Alloy Design & Thermomechanical Processing**
- **Combinatorial Metallurgy & Processing**
- **Atom Probe Tomography** *(funded by Leibniz Award)*
- **Alloys for Additive Manufacturing** *(joint Max Planck - Fraunhofer group)*
- **Adaptive Structural Materials** *(funded by ERC)*
- **Interface Design in Solar Cells** *(funded by BMBF, now at RWTH Aachen)*
- **Biological Composites** *(funded by DFG and Leibniz Award)*

Fig. 3: *Research groups in the Department of Microstructure Physics and Alloy Design.*

steels for automotive applications [75]. Recent projects pursue mechanism-based alloy design strategies [70,72]. The joint design of **novel alloys** using **thermodynamic** and **kinetic predictions** in conjunction with **thermomechanical processing** hence describes the current strategy. A recent field of attention was the analysis of Mn-based model steels [1,14]. Mn is an important alloying element for tuning austenite stability, stacking fault energy, and transformation kinetics. While these effects are exploited particularly in designing steels with **TRIP** and **TWIP** effects, novel alloy concepts introduced by the group combine **martensite-to-austenite reversion** with the TRIP and/or **maraging** effects (maraging: martensite aging) [65,74]. Projects in this field have recently also lead to the discovery of the reason for Mn-related **temper embrittlement** [14] and **confined transformation** effects at lattice defects [1].

The group '**Combinatorial Metallurgy and Processing**' of Hauke Springer designs advanced structural materials along with suited synthesis and processing routes and techniques. The focus lies on steels with superior physical and mechanical properties. Projects explore novel pathways for the compositional and thermo-mechanical **high-throughput** bulk **combinatorial** investigation of structural alloy systems [76-142]. Innovative methods for the **accelerated synthesis**, processing and testing of bulk metallic structural materials are developed and applied, so that the associated metallurgical questions (e.g. alloy- and processing-sensitive changes in strain hardening) and corresponding engineering issues (e.g. texture or joining) can be addressed more efficiently over a wide composition and processing range. Such methods are referred to as '**Rapid Alloy Prototyping**' (RAP) [76]. This approach refers to semi-continuous high-throughput bulk casting, rolling, heat treatment and sample preparation, and currently allows for the evaluation of the mechanical and microstructural properties of up to 50 material conditions (i.e. five different alloy compositions with ten different thermomechanical treatments each) within a few days. This results in a **rapid maturation** of materials and exploration of bulk material libraries for structural materials under consideration of composition and processing. Research fields addressed by this approach are the *in-situ* synthesis of metal matrix steel composites with high stiffness, martensite-to-austenite reversion steels, lightweight Triplex steels [76,83], the development of high strength steels with inherent weldability and methods for optimised microstructure design by the creation of local chemical gradients which are referred to as **vessel microstructure** steels [82].

The group '**Atom Probe Tomography**' of Pyuck-Pa Choi explores compositionally complex structural and functional materials based on the atomic scale information obtained with Atom Probe Tomography (APT) [1-20]. The group was supported by funds from the **Leibniz Award.** It operates two local electrode APT instruments (LEAP 3000X HR, LEAP 5000XS). APT is a high-resolution characterization technique for 3D elemental mapping with near-atomic resolution. It is used for studying nanoscale phenomena such as precipitation, solute clustering, segregation at defects, complexions and partitioning effects [1,69]. An important approach towards better understanding of APT data is the correlation between experiment and theory, conducted in collaboration with the department of J. Neugebauer. Current projects are on high-strength alloys such as **high-Mn steels**, Ni- and Co-based **superalloys** as well as **nanostructured** materials such as cold-drawn **pearlitic steel wires** and **sputter-deposited thin-film multilayers** [1-20,90-111]. Functional materials under investigation are Fe- and Co-based metallic glasses for **magnetic applications**. The group also studies **semiconductors** for **photovoltaic** applications in close collaboration with the group of O. Cojocaru-Mirédin (Interface Design in Solar Cells) [90-93]. Special attention is placed on **correlative TEM and APT** for the joint structural and chemical analysis of atomic-scale microstructure features.

The new group on '**Alloys for Additive Manufacturing**' of Eric Jägle was established in 2015 [94]. While particularly **Laser Additive Manufacturing** (LAM) is well-established to produce metallic parts, the optimization of alloys and the design of new materials tailored for LAM are still missing. Established alloys currently in use do not exploit the opportunities inherent in this technique, leaving a gap towards its further development. Funding for the group comes from the joint Max-Planck Society/ Fraunhofer Society research project “AProLAM” - **Advanced Alloys and Process Design for Laser Additive Manufacturing of Metals**. In this project, the two partners Max-Planck-Institut für Eisenforschung (MPIE) and Fraunhofer Institute for Laser Technology (ILT) work together on the development of alloys for the LAM process and at the same time on the adaptation of the LAM process for the synthesis of **new alloys**.

The group for ‘**Adaptive Structural Materials**’ of Cem Tasan develops novel experimental-theoretical tools to understand micro-mechanisms governing macro-properties and design property-optimized novel structural alloys [35-41]. The group is linked to the theory group of B. Grabowski (Department of Computational Materials Design) and sponsored by an **ERC Advanced Co-Investigator Grant** of D. Raabe and J. Neugebauer. Conventional **hardening mechanisms** lead to a decrease in ductility. With the development of **adaptive structural materials** (ASM) the group’s key idea is based on designing, synthesizing and characterizing **intrinsic phase instability**. The philosophy behind that is to either incorporate dispersed phases that are close or even beyond their mechanical and thermodynamic **stability limit** into otherwise stable bulk alloys or to design the bulk material itself such that it is at the verge of mechanical/thermodynamic stability. In either case the phases transform under loading into secondary phases (i.e. martensite) or extended defects (e.g. twin bundles). The group combines quantum-mechanically guided design with *in-situ* experimentation. On the theory side, the group of B. Grabowski has developed approaches to accurately describe finite temperature effects from first principles [37,95-99]. On the experimental side the group employs (i) various metallurgical production and processing routes, (ii) multi-scale characterization down to atomic resolution and mechanical testing, and (iii) high-resolution *in-situ* characterization of phase transformations and deformation mechanisms [72,145]. The latter is of particular importance for ASMs, since the determination of the stable regimes of the introduced unstable phases is in most cases only possible through such *in-situ* analysis. The group leader Cem Tasan has accepted a **faculty position at MIT** in Cambridge, USA, starting January

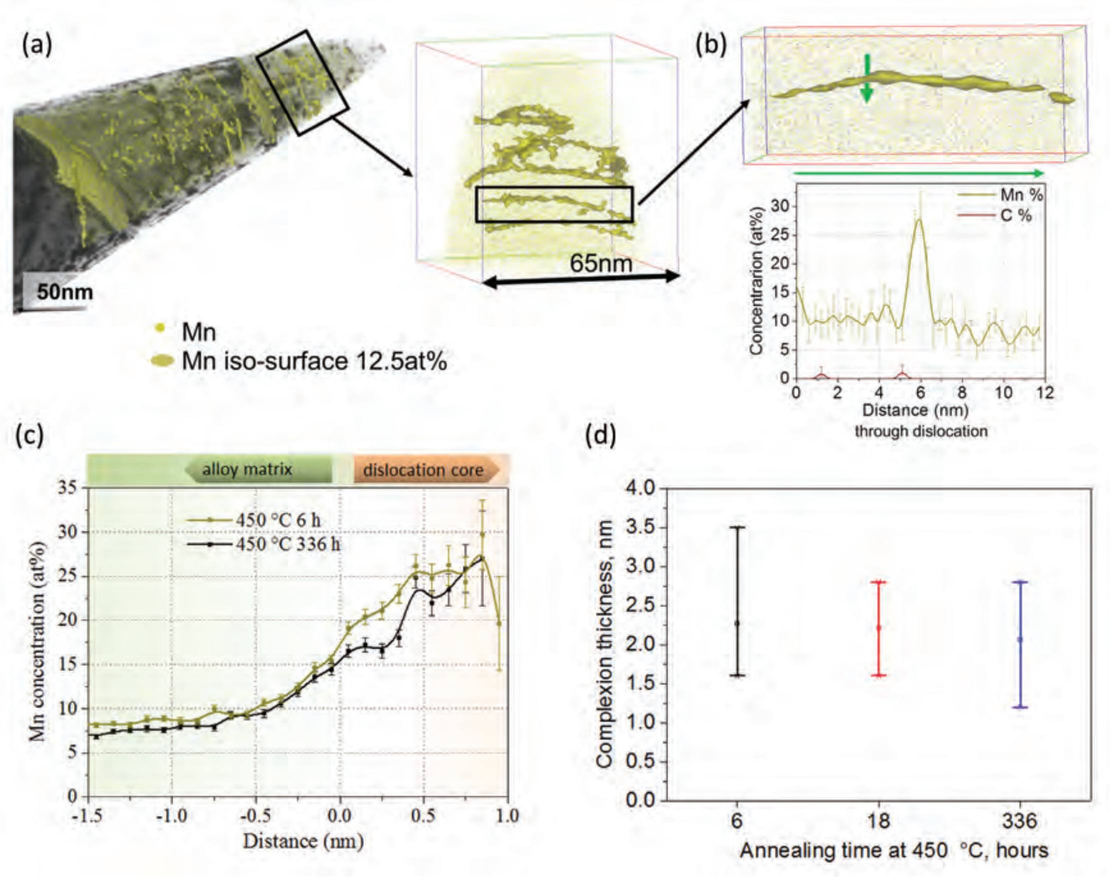


Fig. 4: *Fe-9 at. % Mn solid solution, 50% cold-rolled and annealed at 450°C for 6 hours to trigger Mn segregation [1]. (a) Correlative TEM - APT. (b) Subregion and 1D compositional profile along the dislocation line. (c) Proximity histograms. (d) Prolonged aging neither affects size nor composition of the austenitic dislocation core regions which is one of the most characteristic features of linear complexions.*

2016. The work will in future be pursued in close collaboration with his group at MIT.

The group '**Interface Design in Solar Cells**' of Oana Cojocaru-Mirédin aims to understand the relationship between the chemical, electrical, and structural properties of interface-dominated solar cells. Focus is placed on **multicrystalline silicon** (m-Si) solar cells, and $Cu_2ZnSnSe_4$ (CZTS) and Cu(In,Ga)Se_2 (CIGS) **thin-film solar cells** because of their relatively **high efficiency**. To better understand these materials the group performs correlative studies on specific regions using joint EBSD / TEM, electron beam-induced current (**EBIC**)/ **cathodoluminescence**, and **APT** [90-93]. The mission is to optimize solar cell efficiency based on the 3D chemical analysis at the atomic-scale. The atomic redistribution of the impurities at the internal interfaces (grain boundaries and p-n junction) may affect the efficiency of a solar cell. For example, the efficiency of a CIGS solar cell has been improved by almost 50% only by Na doping (~ 0.1 at.%) inside the absorber layer. Furthermore, it was observed that this increase in the efficiency can be directly correlated with the Na segregation at the CIGS grain-boundaries. The group is financed by the federal ministry "Bundesministerium für Bildung und Forschung" (NanoMatFutur competition). The group leader Oana Cojocaru-Mirédin has recently accepted a permanent group leader position at RWTH Aachen. Corresponding topics will in future be pursued in close collaboration.

The group '**Biological Composites**' of Helge Fabritius works on the interactions of structure, composition and properties of **biological materials**. The group was established in 2008 from funds of the **Leibniz Award**. Projects aim to reveal how nature designs and optimizes materials through modifications in structure and composition from the molecular level up to **specialized tissues** and functional parts. The group pursues an integrative approach combining **experiments and simulations** based on detailed structural characterization [100-108]. Recently, the group works on the development of **bio-inspired and biomimetic** materials such as **optical sensors** [102] and **dental materials** [100,103]. The main model material in the group is the Arthropod cuticle [101]. Its structure consists of fibrillary chitin and proteins independent of the exact location. Owing to its double function as integument and exoskeleton, the cuticle fulfils different functions that require a variety of physical properties. These can be mechanical, optical, and also combinations of several properties within the same skeletal element such as the transitions between the elastic arthrodial membranes and the rigid mineralized cuticle of limb segments. Other model materials include vertebrate **bones** and **teeth**, specifically those of sharks [100,103,105].

Main Research Interests

The objectives of the research groups and their core competences were described above. Here we present our **recent progress** in a number of **key interdisciplinary areas of interests** in the department which are **jointly pursued** by members of different groups including also members from other departments. More specific **scientific details** about some of these projects are given in the section **"Interdepartmental Research Activities - Selected Highlights".**

Segregation Engineering: Mechanical-chemical effects at lattice defects - from segregation to manipulation

Dislocations and **interfaces** influence mechanical, functional, and kinetic properties of alloys. They can be manipulated via **solute decoration** enabling changes in energy, mobility, structure, and cohesion or even promoting local phase transformation. In the approach which we refer to as **'segregation engineering**' solute decoration is not regarded as an undesired phenomenon but is instead utilized to manipulate specific defect structures, compositions and properties [1,14,69,74].

For instance we found that **grain boundary (GB) segregation engineering** and local austenite reversion can turn interface embrittlement into toughness [14]. In a Fe-9 wt.% Mn martensite we studied **grain boundary embrittlement** in the quenched and tempered state. While solute Mn directly embrittles martensite grain boundaries, reversion of martensite back to austenite at grain boundaries cleans the interfaces from solute Mn by partitioning the Mn into the newly formed austenite, hence restoring **impact toughness** (see p. 50; see p. 173).

Fig. 4 shows the discovery of a chemical and structural state confined to dislocation cores which we refer to as **linear complexion** [1]. Dislocations attract solutes according to the Gibbs isotherm. The concept of interface complexions extends the classical isotherm to **interface-stabilized states** that have a structure and composition different from that of the matrix and remain confined in the region where they form. We observed such a phenomenon at edge dislocations in a binary Fe-9 at.% Mn alloy in which a stable confined austenite structure forms in an otherwise martensitic crystal. This is a 1D analog of the previously observed **complexions** that were observed at planar defects (see p. 50; see p. 181).

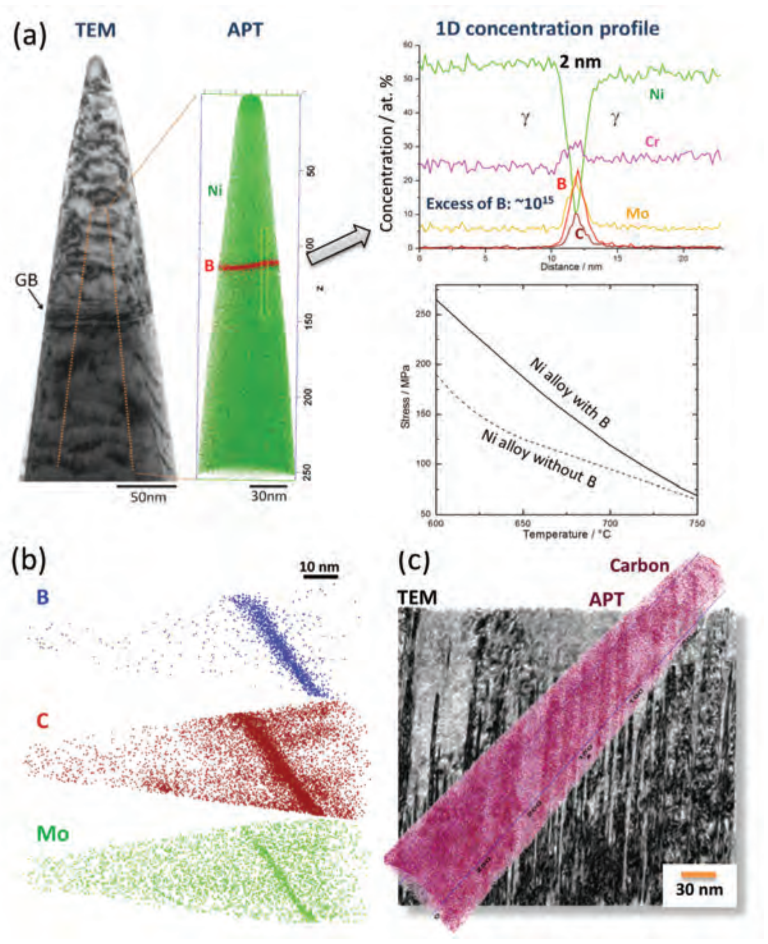


Fig. 5: *Segregation of B to a high angle GB in Ni-alloy 617. B improves - via improved GB cohesion and GB precipitation - the rupture strength as shown in terms of the comparison of alloy 617 (Nicrofer5520Co) and the B-doped variant alloy 617B (Nicrofer5520CoB) in the range between 600 to 750°C (105h) [110]. Segregation of B is also found at prior austenite grain boundaries in quenched martensitic steels [73]. In as-quenched Fe-C martensite the cooling rates are typically too slow to entirely freeze C in at its original positions. Hence, C relaxes to lath interfaces [2].*

Fig. 5 shows examples where **Interface Segregation Engineering** was used to **enhance grain boundary cohesion**. An example is B doping of creep-resistant polycrystalline **Ni-based alloys** used for power plant applications. Fig. 5 shows alloy 617 where **B segregation** on **grain boundaries** was revealed by using **correlative TEM-APT**, leading to enhanced grain boundary cohesion and the promotion of the formation of precipitates [110]. B segregation was also found at **prior austenite grain boundaries** in quenched **martensite**. In these materials we found that B and Mo segregate only to prior austenite grain boundaries but are absent at martensite–martensite interfaces. C segregated both at prior austenite grain boundaries and at martensite–martensite boundaries. Even in conventional as-quenched **Fe-C martensite** cooling rates are slow enough to allow C relaxation to the lath interfaces.

Microstructure-sensitive analysis of corrosion and hydrogen embrittlement

A main challenge in **corrosion science** consists in identifying the relations between **microstructure features** and the associated electrochemical or physical reactions, respectively, such as **oxidation** [11-115] and **hydrogen embrittlement** [116-121] (see p. 185). In this context, measurements including sufficient spatial resolution of the associated phenomena down to the lattice defect scale are still hard to realize. Yet, the role of individual lattice defects and surface features together with a characterization of their individual structural and chemical state is essential for understanding corrosion and the resulting decay and failure mechanisms. Specifically **site-specific microstructure and composition characterization** is of great relevance. Instrumentation we use in this context are **correlative atom probe tomography**, **Scanning Kelvin Probe** mapping (together with M. Rohwerder) in conjunction with EBSD and ECCI as well as **nanoSIMS** maps. Fig. 6 shows a study on the role of **grain boundaries in the initial oxidation** behaviour of **austenitic stainless steel** at 700°C in air with 20% water vapor for power plant applications [114].

We also compared local hydrogen uptake and release rates by multi-scale **hydrogen mapping** with **spatial resolution** in a Ni-Nb two-phase model alloy, Fig. 7, focusing on two aspects: (1) mapping the **hydrogen distribution** with spatial resolution for establishing the correspondence between desorption profiles and desorption sites, and (2) correlating the obtained results with mechanical testing to reveal the degradation mechanisms. The trapping states were analyzed by **thermal desorption spectroscopy** (TDS). The Ag-decoration method revealed rapid effusion of hydrogen from the matrix, the kinetics of which was spatially resolved through **Scanning Kelvin Probe Force Microscopy** (SKPFM) by the group of M. Rohwerder. The hydrogen release from the matrix steadily decreased until about 100 h and then was taken over by the precipitation phase (δ-Ni$_3$Nb). The deuterium distribution in the microstructure was studied by **Secondary Ion Mass Spectrometry** (SIMS) (see p. 185).

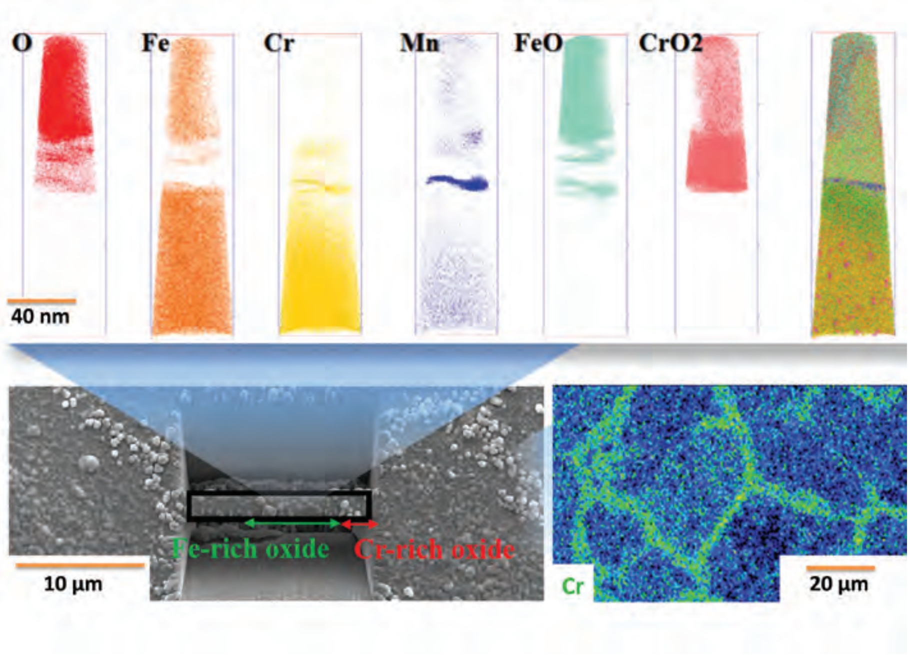


Fig. 6: *Multiscale characterization of microstructure-specific oxidation behaviour (at 700°C) conducted on an austenitic stainless steel [114].*

Fig. 8 shows **hydrogen-induced cracking** at grain and twin boundaries in a Fe-18Mn-1.2C (wt.%) austenitic steel [117-120]. The tensile ductility was drastically reduced by hydrogen charging during tensile testing. The fracture mode was mainly intergranular fracture, though transgranular fracture was also observed. **Transgranular fracture** occurred parallel to the primary and secondary deformation twin boundaries, as confirmed by EBSD and ECCI. The microstructural observations indicated that cracks were initiated at grain boundaries and twin boundaries.

Alloy design for 3D printing and for strong and ductile multicomponent alloys

The **design of novel alloys** is a key challenge for several reasons: First, using thermomechanical processing alone for the design of microstructures is an efficient but limited approach. Including a higher variety of solution and transformation phenomena by **alloy modifications** opens the field of material design beyond the scope offered by processing alone. On the other hand, introducing new compositions without systematic **thermomechanical treatment** studies does also not provide sufficient depth in structural alloy design [122-133]. Hence, we increasingly merge the two disciplines. Second, novel tools such as *ab initio* simulations and kinetic Monte Carlo methods in conjunction with statistical tools such as **ThermoCalc** and **Dictra** render alloy design increasingly accessible to quantitative predictions

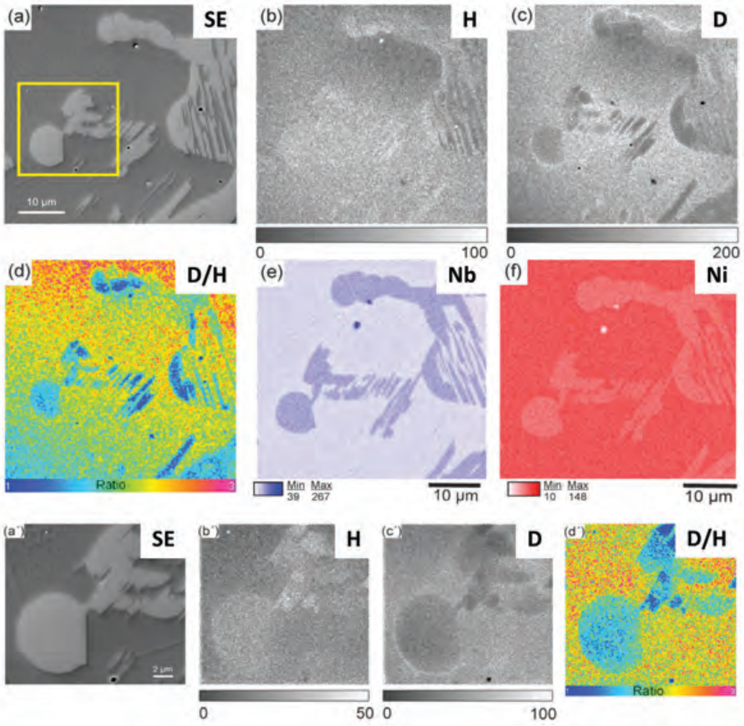


Fig. 7: *NiNb specimen charged with H: (a) SE image and secondary ion maps of (b) H, (c) D, and (d) (2D-/1H-). (e), (f) EDX map of Nb and Ni, respectively. (a´)-(d´) Magnified regions as marked in (a). NanoSIMS in collaboration with L. Yedra and S. Eswara, Luxembourg Institute of Science and Technology.*

[134-138]. Third, high-throughput alloy design methods enable probing wider composition, forming and heat treatment ranges [76-83].

A field of interest for **alloy design** is **Laser Additive Manufacturing** (LAM) [94]. Fig. 9 shows an example where precipitation and austenite reversion in a LAM produced maraging steel were studied. The motivation for this project is that materials produced by selective laser melting (SLM) experience a thermal history that is markedly different from that encountered by conventionally produced materials. In particular, a very high cooling rate from the melt is combined with cyclic reheating upon deposition of subsequent layers. Using APT, we investigated how this thermal history influences the phase-transformation behaviour of LAM synthesized maraging steels (Fe-18Ni-9Co-3.4Mo-1.2Ti) (see p. 25).

We also study **massive solid solution** materials, an alloy class referred to as **high entropy alloys (HEAs)**. We work specifically on materials where the configurational entropy is below its maximum value, Fig. 10 [95,139-144]. The concept was realized in the form of **non-equiatomic multi-component** CoCrFeMnNi alloys produced by rapid alloy prototyping. Their microstructures exhibit a random elemental distribution in a single FCC phase which deforms by planar slip, leading to excellent ductility. We use compositional variations to tune the stacking fault energy and hence the associated transformation phenomena which act as main mechanisms for designing high strain hardening rates (see p. 50).

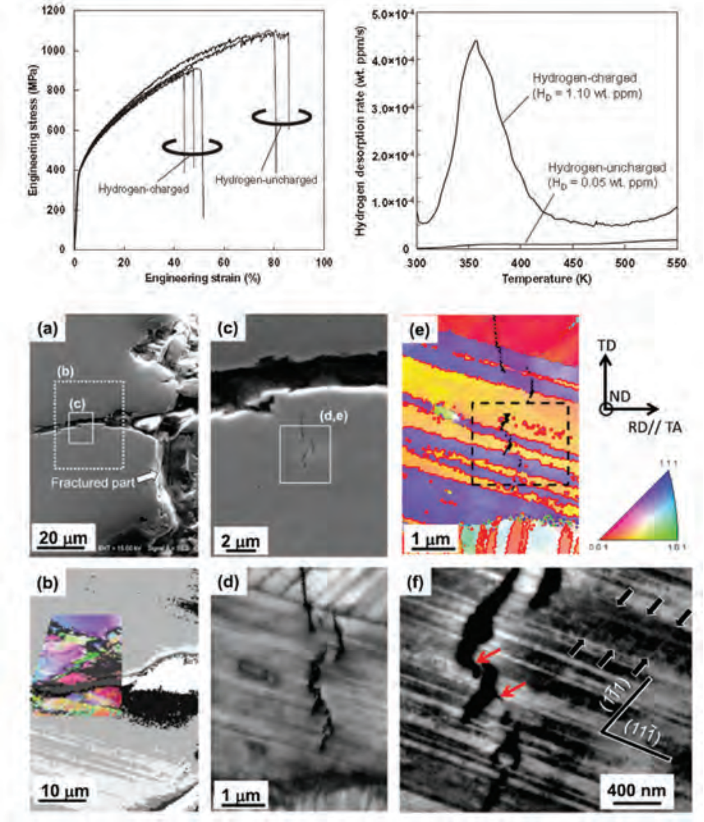


Fig. 8: *Hydrogen embrittlement in an Fe-18Mn-1.2C (wt.%) TWIP steel [119]. Tensile ductility was drastically reduced by H. Top row: Stress–strain curves and H desorption rates in a steel with and without H charging. Bottom images: micrographs near the crack. (a) SEI micrograph. (b) Texture map superimposed on detector signal image. (c) Magnified image of the area within the white lines in (a). (d, e) Image quality and texture maps of area marked by white lines in (c). (f) ECCI corresponding to the area within the black broken lines in (e) [117-120].*

Phase transformations

In conjunction with the **interface segregation engineering** approach discussed above [14,67,109] we developed a class of novel steels which we refer to

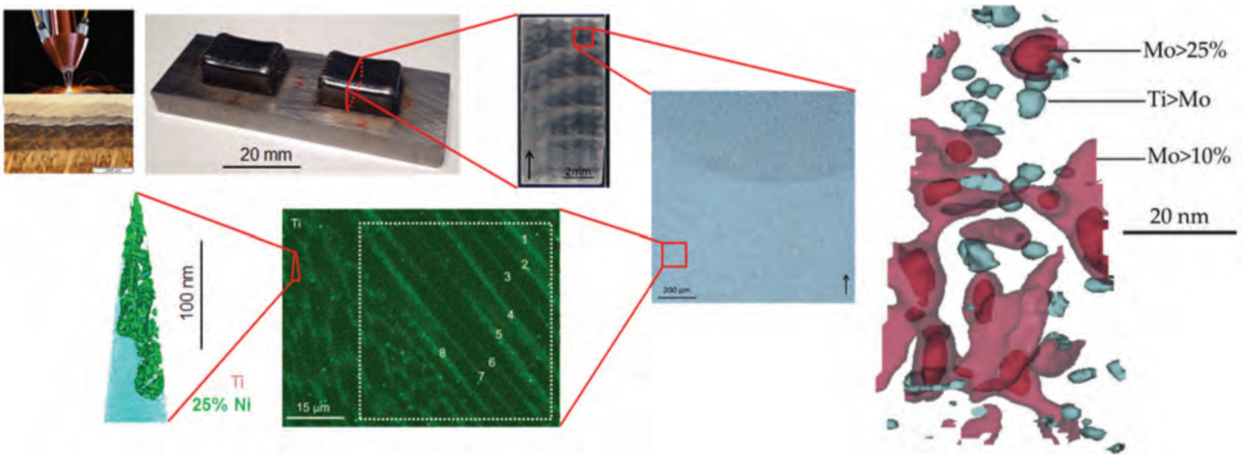


Fig. 9: *Multiscale structural and chemical analysis of maraging steel microstructures obtained from Laser Additive Manufacturing. The APT data set on the right hand side provides three isoconcentration surfaces for identifying the stoichiometry of the different nanoprecipitates [94].*

as '**Martensite Reversion Steels**' [65,68,69]. These are ductile **micro- and nanolaminate alloys** that are formed by reheating as-quenched martensite steels (e.g. Fe-Mn, Fe-Ni, Fe-C, maraging or Fe-Cr-C steels) so that segregation-driven reversion from martensite back to austenite occurs at internal interfaces, preferably at the **lath interfaces**, Fig. 11 [145]. The size, elemental partitioning, shape and position of the reversed phases determine the mechanical properties of the bulk compound. These alloys resemble intrinsically formed damask alloys, enabled by a segregation, reversion and partitioning heat treatment. Preceding plastic deformation can profoundly enhance the effect as it provides additional nucleation sites for reversion (see p. 50).

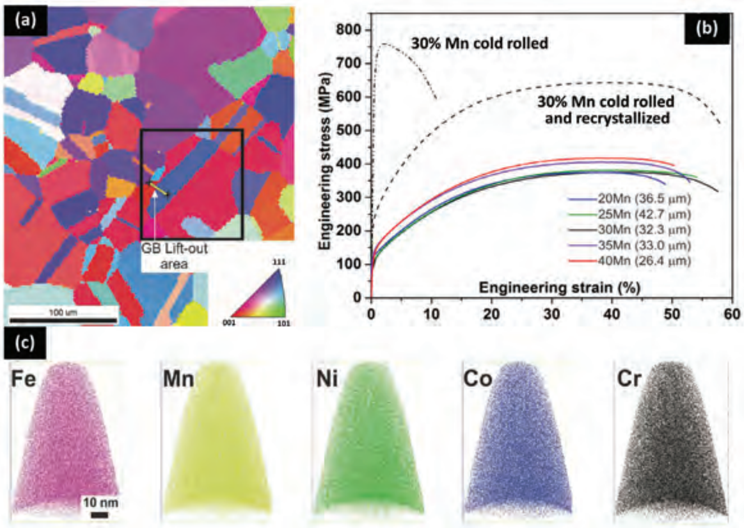


Fig. 10: *Fe_{62}-$Mn_xNi_{30}Co_6Cr_2$ non-equiatomic high entropy alloys (x: variation in Mn) (a) Inverse pole figure map showing the APT lift out region. (b) Stress-strain curves of all alloys: the 30 at.% Mn alloy is shown in cold rolled (64%) and recrystallized (900°C, 10 min) states. (c) APT reveals the materials' compositional homogeneity [95,139-144].*

Similar phenomena occur in **Ti-Mo and Ti-Fe alloys** where β-phase films form between the α-lath portions by a reversion heat treatment, Fig. 12 [132]. The phase transformation and reversion kinetics between the hexagonal α-phase and the bcc β-phase enable the design of laminate microstructures leading to excellent mechanical properties. We studied the effects of different types of reversion treatments in a **binary Ti-4Mo (wt%) model alloy**. We observed a broad variety of microstructure formation mechanisms including diffusion driven allotropic phase transformations as well as shear and/or diffusion dominated modes of martensitic transformations, leading to a wealth of microstructure design options in a simple binary Ti alloy (see p. 50).

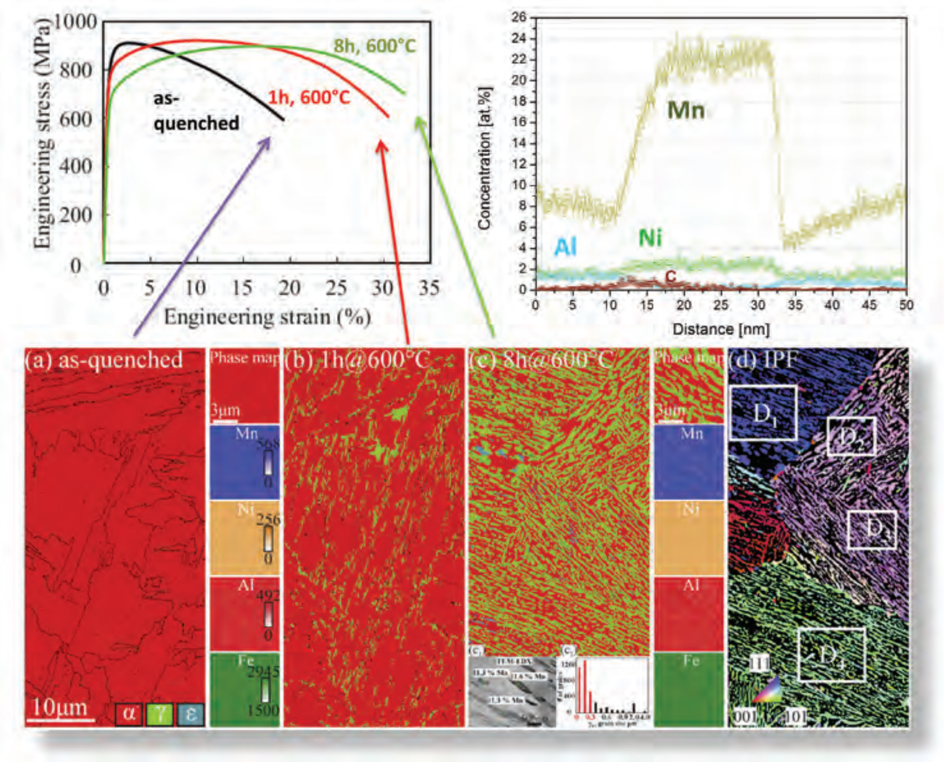


Fig. 11: *Grain boundary segregation followed by confined reversion transformation (revealed by APT) from the as-quenched martensite into austenite enables the design of damask-type martensite-austenite nanolaminate steels where the solute decorated lath interfaces transform back to austenite [145].*

Multilayer nanolaminates

Multilayer nanolaminates are capable of **reconciling strength and ductility** and/or providing toughness or hardness to **substrate surfaces**. We study the nanostructure evolution of metallic crystal-glass [3,8,20] and multi-nitride laminates [89,146] with respect to their mechanical, thermal and compositional stability when exposed to **thermal and mechanical loading**. As

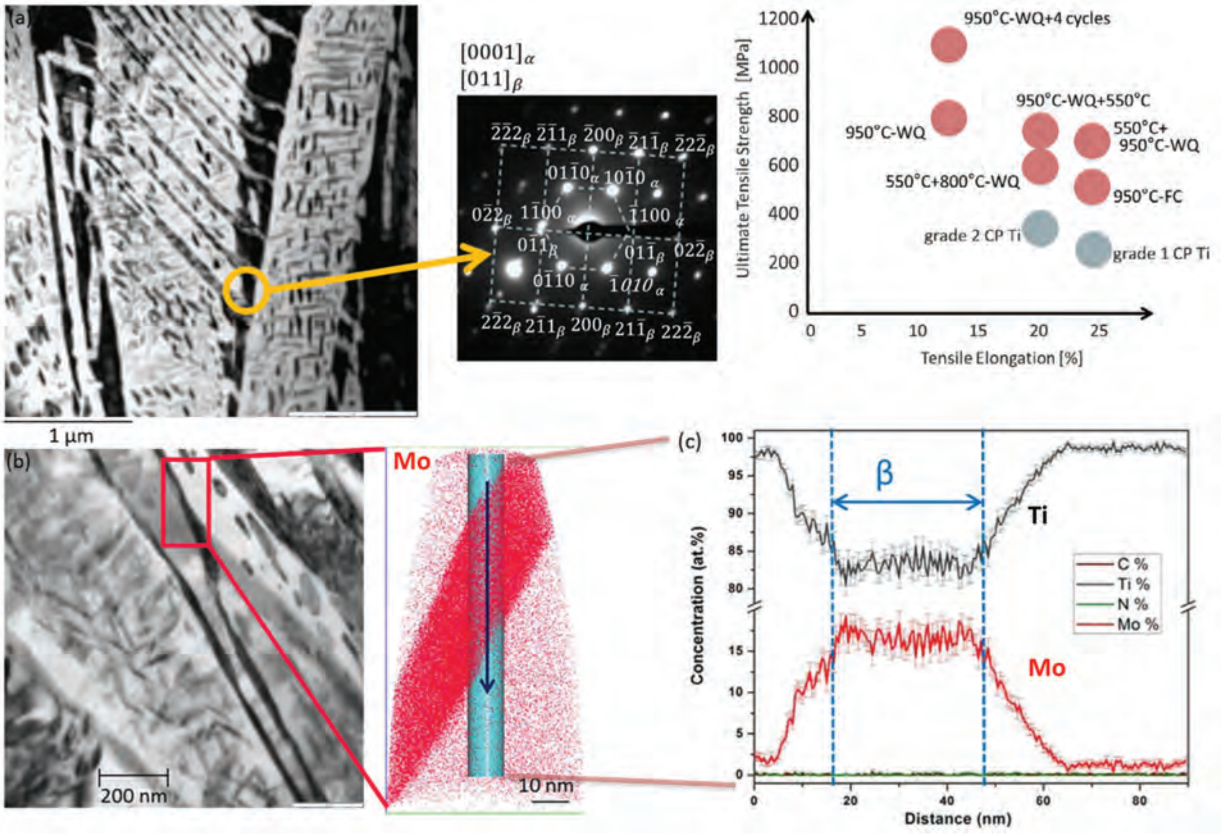


Fig. 12: *(a) Bright-field TEM micrograph and selected area diffraction pattern depicting the near-Burgers orientation relationship observed between the α (hcp) and β (bcc) phases in Ti-4Mo after heat treatment 950°C-WQ + 550°C. (b) TEM bright field image, APT elemental map showing Mo atoms and (c) the corresponding 1-D concentration profile (bin width 0.5 nm) across the Mo enriched layer (cylindrical region of interest in (b)) showing very pronounced partitioning of Mo (red) of about 20 at% into a 20 nm thick b lamellar zone, enhancing its stability against phase transformation. Upper right image: Tensile mechanical properties of Ti-4wt.%Mo after different heat treatments; (CP: commercial purity standard)* [132].

one model system we chose **crystalline-amorphous** Cu–CuZr **nanolaminates** [3,8,20]. We conducted indentation experiments on 10 nm nanocrystalline Cu–100 nm amorphous CuZr multilayers, Fig. 13. By **correlative APT-TEM** we found that crystallographic slip bands in the Cu layers coincide with non-crystallographic shear bands in the amorphous CuZr layers. Dislocations from the crystalline layers drag Cu atoms across the interface into the CuZr layers. Also, crystalline Cu blocks were sheared into the CuZr layers.

In another project, conducted together with J. Neugebauer, we performed **joint APT structural data analysis and quantum-mechanical calculations** in a theory-guided design approach to identify **nanolaminate superlattices** with **extreme-stiffness**, Fig 14 [147]. These superlattices can contain metastable phases which are stabilized by epitaxial constraints. The study combines theoretical and experimental methods to optimize the elastic properties of AlN/CrN superlattices with 4 nm bilayer period. CrN stabilizes AlN in a metastable B1 (rock salt) cubic phase only in the form of a layer that is very thin, up to a few nm. The *ab initio* predicted Young's modulus (428 GPa) along [001] is in excellent agree-ment with corresponding values from nano-indentation (408±32 GPa) (see p. 50).

Micromechanics of high-mechanical contrast materials

Multiphase microstructures containing phases with **high mechanical contrast** are essential in alloy design [35,36,55,56]. Particularly **dual-phase (DP) steels** take a prominent position among high-strength steels, but they are prone to failure. In a series of studies we explored (a) the microstructure evolution during processing, (b) conducted detailed experimental characterization of the micromechanical behaviour and phase co-deformation, and (c) simulated the micromechanical and coarse grained material behaviour. Fig. 15 shows some of the main resulting trends to guide future DP design efforts [40] (see p. 50).

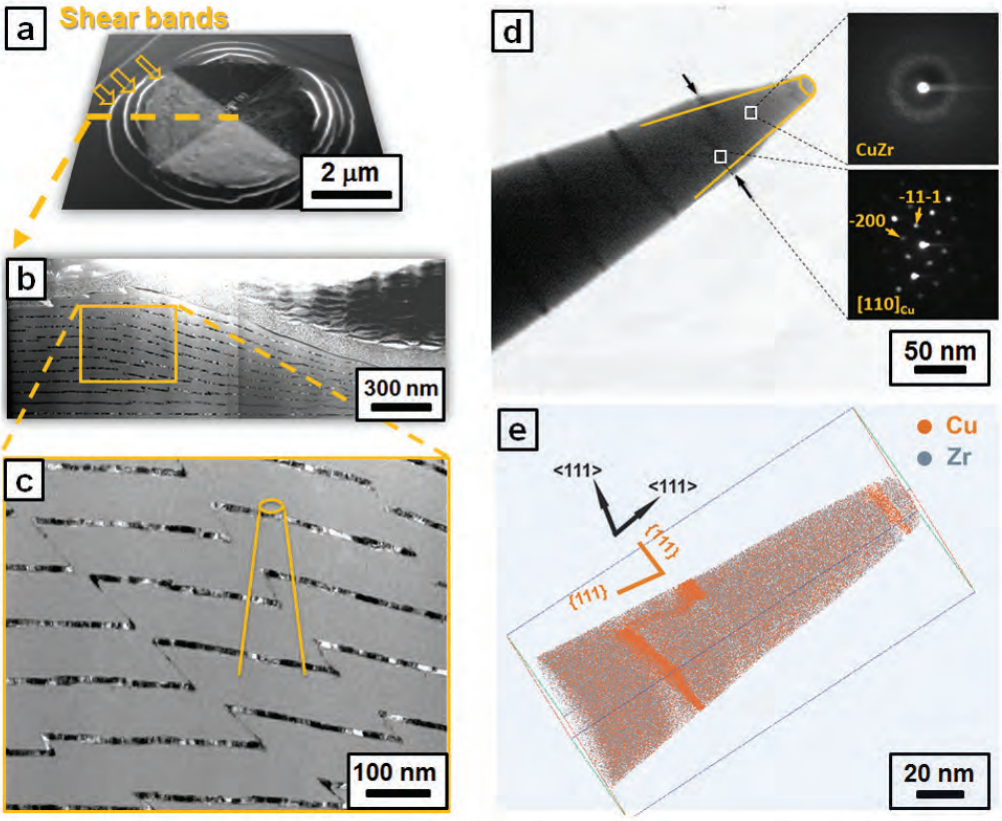


Fig. 13: *(a) SEM view of indented CuZr/Cu nanolaminates. (b) Shear bands. (c) Bright field TEM image of shear bands. Yellow lines mark a region studied by APT. (d) Bright field TEM of an APT tip with CuZr and Cu nanobeam diffraction. Arrows show the shear band region. (e) APT reconstructed volume from the exact APT tip shown in (d)* [3,8,20].

Main Recent Breakthroughs

In several cases we achieved breakthroughs during the past years. While some resulted from **unexpected discoveries** [1], others were harvested from **long term and systematic developments** [24,26,42].

Regarding method development we have established a versatile experimental protocol for conducting site-specific sample extraction in conjunction with **correlated TEM-APT characterization** [1-5,18]. This approach enables profound insights into the interrelationships between structure and composition in complex microstructures at near atomic scale. Examples where this approach enabled basic new insights are the discovery of **linear complexions** [1], atomic-scale analysis of **segregation** phenomena in 5D crystallographic space [5], the observation of para-equilibrium partitioning in **quench-partitioning** steels [128] and interface phase formation in **high entropy alloys** [139].

Similar progress was enabled by rendering the **Electron Chaneling Contrast Imaging** method quantitative by combining it with controlled diffraction conditions (cECCI) [25-27]. It allows the direct observation of crystal defects such as dislocations or stacking faults close to the surface of bulk samples. This technique, which has similarities to dark field TEM, is applied in a SEM and allows probing the first 50–100 nm of material below the surface.

Substantial progress was also made in the field of **mapping hydrogen** with high spatial resolution, hence, correlating trapping sites and damage events with local microstructure features.

In the field of **simulation** substantial progress was made in the field of joint polycrystal and multiphysics modeling. The corresponding software package developed during the past 15 years was released to the public domain as **Düsseldorf Advanced MAterials Simulation Kit** (**DAMASK**) and can be downloaded at **http://damask.mpie.de**. It is used by a number of research groups worldwide [42]. Regarding alloy design we have made substantial progress by introducing the concept of **non-equiatomic high entropy alloys** [95,140-144] and the use of **interstitial alloying** in these materials [81].

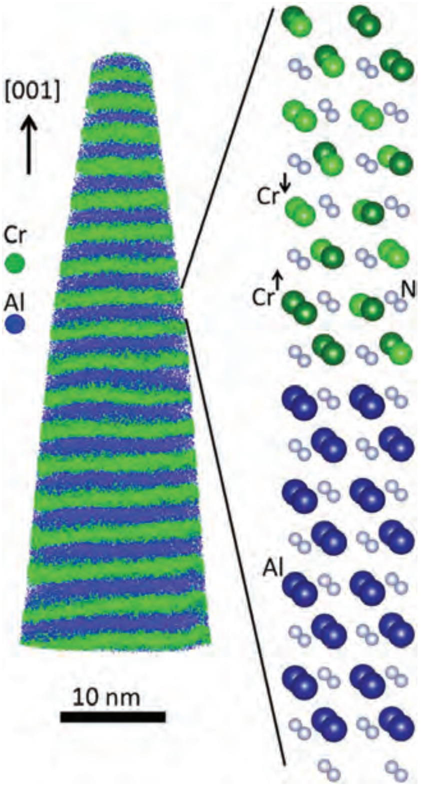


Fig. 14: *Spatial distribution of Cr and Al in an AlN/CrN superlattice measured by APT (left) and the computational model derived from these data (right) for identifying nanolaminate superlattices with extreme-stiffness [147].*

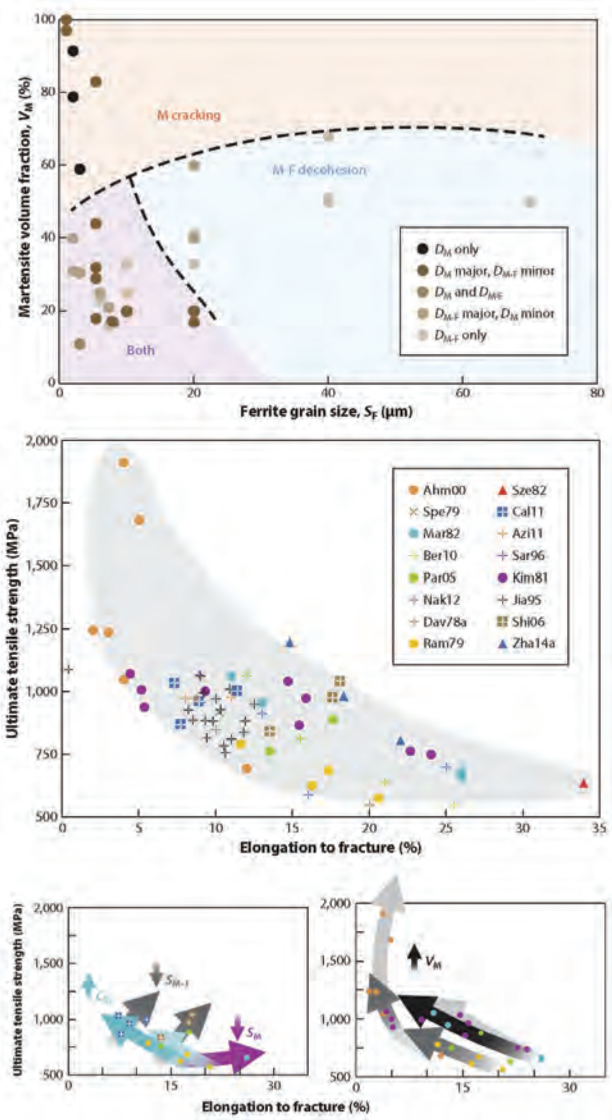


Fig. 15: *Dual-phase (DP) steels: Damage analysis reveals the effects of ferrite grain size (SF) and martensite volume fraction (VM) on the type of damage: martensite cracking (DM) and martensite-ferrite decohesion (DM−F). F and M indicate ferrite and martensite, respectively. Middle row: strength – ductility combinations compiled for a large number of DP steels. The original data and references are provided in [40]. Bottom row: Several trends due to microstructure effects. Abbreviations: CM, martensite carbon content; SM+F, martensite and ferrite grain size; SM, martensite grain size; VM, martensite volume fraction [40].*

References

1. Kuzmina, M., Herbig, M., Ponge, D., Sandlöbes, S., Raabe, D. Linear complexions: Science (2015) 349 (6252), 1080-1083.
2. Morsdorf, L., Tasan, C.C., Ponge, D., Raabe, D. Acta Materialia (2015) 95, 366-377.
3. Guo, W., Jägle, E.A., Choi, P.-P., Yao, J., Kostka, A., Schneider, J.M., Raabe, D.: Physical Review Letters (2014), 113 (3), art. no. 035501.
4. Song, W., Choi, P.-P., Inden, G., Prahl, U., Raabe, D., Bleck, W.: Metallurgical and Materials Transactions A (2014), 45 (2), 595-606.
5. Herbig, M., Raabe, D., Li, Y.J., Choi, P., Zaefferer, S., Goto, S.: Physical Review Letters (2013), 112 (12), art. no. 126103.
6. Seol, J.-B., Raabe, D., Choi, P., Park, H.-S., Kwak, J.-H., Park, C.-G.: Scripta Materialia (2013), 68 (6), 348-353.
7. Isik, M.I., Kostka, A., Yardley, V.A., Pradeep, K.G., Duarte, M.J., Choi, P.P., Raabe, D., Eggeler, G.: Acta Materialia (2015), 90, 94-104.
8. Guo, W., Yao, J., Jägle, E.A., Choi, P.-P., Herbig, M., Schneider, J.M., Raabe, D.: Materials Science and Engineering A (2015), 628, 269-280.
9. Song, W., Von Appen, J., Choi, P., Dronskowski, R., Raabe, D., Bleck, W.: Acta Materialia (2013), 61 (20), 7582-7590.
10. Prakash, A., Guénolé, J., Wang, J., Müller, J., Spiecker, E., Mills, M.J., Povstugar, I., Choi, P., Raabe, D., Bitzek, E.: Acta Materialia (2015), 92, 33-45.

11. Matuszewski, K., Rettig, R., Matysiak, H., Peng, Z., Povstugar, I., Choi, P., Müller, J., Raabe, D., Spiecker, E., Kurzydłowski, K.J., Singer, R.F.: Acta Materialia (2015), 95, 274-283.
12. Seol, J.-B., Raabe, D., Choi, P.-P., Im, Y.-R., Park, C.-G.: (2012) Acta Materialia, 60 (17), pp. 6183-6199.
13. Aboulfadl, H., Deges, J., Choi, P., Raabe, D.: Acta Materialia (2012), 86, 34-42.
14. Kuzmina, M., Ponge, D., Raabe, D.: Acta Materialia (2015), 86, 182-192.
15. Povstugar, I., Choi, P.-P., Neumeier, S., Bauer, A., Zenk, C.H., Göken, M., Raabe, D.: Acta Materialia (2014), 78, 78-85.
16. Li, Y.J., Kostka, A., Choi, P., Goto, S., Ponge, D., Kirchheim, R., Raabe, D.: Acta Materialia (2015), 84, 110-123.
17. Mattern, N., Han, J.H., Pradeep, K.G., Kim, K.C., Park, E.M., Kim, D.H., Yokoyama, Y., Raabe, D., Eckert, J. Journal of Alloys and Compounds (2014), 607, 285-290.
18. Li, Y., Raabe, D., Herbig, M., Choi, P.-P., Goto, S., Kostka, A., Yarita, H., Borchers, C., Kirchheim, R. Physical Review Letters (2014), 113 (10), art. no. 106104.
19. Stoffers, A., Cojocaru-Miredin, O., Breitenstein, O., Seifert, W., Zaefferer, S., Raabe, D.: 2014 IEEE 40th Photovoltaic Specialist Conference, PVSC 2014, art. no. 6925089, 42-46.
20. Guo, W., Jägle, E., Yao, J., Maier, V., Korte-Kerzel, S., Schneider, J.M., Raabe, D.: Acta Materialia (2014), 80, 94-106.
21. Ram, F., Zaefferer, S., Raabe, D.: Journal of Applied Crystallography (2014), 47 (1), 264-275.
22. Ram, F., Zaefferer, S., Jäpel, T., Raabe, D.: Journal of Applied Crystallography, (2015) 48, 797-813.
23. Cédat, D., Fandeur, O., Rey, C., Raabe, D.: Acta Materialia (2012), 60 (4), pp. 1623-1632.
24. Konijnenberg, P.J., Zaefferer, S., Raabe, D.: Acta Materialia 99 (2015), 402–414.
25. Gutierrez-Urrutia, I., Raabe, D.: Acta Materialia (2012), 60 (16), pp. 5791-5802.
26. Zaefferer, S., Elhami N.: Acta Materialia 75 (2014), 20–50.
27. Gutierrez-Urrutia, I., Zaefferer, S., Raabe, D.: Scripta Materialia (2009), 61 (7), 737-740.
28. Gutierrez-Urrutia, I., Raabe, D.: Scripta Materialia (2013), 69 (1), 53-56.
29. Steinmetz, D.R., Jäpel, T., Wietbrock, B., Eisenlohr, P., Gutierrez-Urrutia, I., Saeed-Akbari, A., Hickel, T., Roters, F., Raabe, D.: Acta Materialia (2013), 61 (2), 494-510.
30. Gutierrez-Urrutia, I., Zaefferer, S., Raabe, D.: JOM (2013), 65 (9), 1229-1236.
31. Yan, F.K., Tao, N.R., Archie, F., Gutierrez-Urrutia, I., Raabe, D., Lu, K.: Acta Materialia (2014), 81, 487-500.
32. Wen, Y.H., Peng, H.B., Raabe, D., Gutierrez-Urrutia, I., Chen, J., Du, Y.Y.: Nature Communications (2014), 5, art. no. 5964.
33. Nellessen, J., Sandlöbes, S., Raabe, D.: Acta Materialia (2015), 87, 86-99.
34. Zhang, J.-L., Zaefferer, S., Raabe, D.:Materials Science and Engineering A (2015), 636, 231-242.
35. Tasan, C.C., Hoefnagels, J.P.M., Diehl, M., Yan, D., Roters, F., Raabe, D.: International Journal of Plasticity (2014), 63, 198-210.
36. Tasan, C.C., Diehl, M., Yan, D., Zambaldi, C., Shanthraj, P., Roters, F., Raabe, D.: Acta Materialia (2014), 81, 386-400.
37. Lai, M.J., Tasan, C.C., Zhang, J., Grabowski, B., Huang, L.F., Raabe, D.: Acta Materialia (2015), 92, 55-63.
38. Yan, D., Tasan, C.C., Raabe, D.: Acta Materialia (2015), 96, 399-409.
39. Eisenlohr, A., Gutierrez-Urrutia, I., Raabe, D.: Acta Materialia (2012), 60 (9), 3994-4004.
40. Tasan C.C., M. Diehl, D. Yan, M. Bechtold, F. Roters, L. Schemmann, C. Zheng, N. Peranio, D. Ponge, M. Koyama, K. Tsuzaki, and D. Raabe: Annual Review of Materials Research (2015), vol. 45, no. 1, 391–431.
41. Lai, M.J., Tasan, C.C., Raabe, D.: Acta Materialia (2015), 100, 290-300.
42. Roters, F., Eisenlohr, P., Kords, C., Tjahjanto, D.D., Diehl, M., Raabe, D.: Procedia IUTAM (2012), 3, 3-10.
43. Jia, N., Roters, F., Eisenlohr, P., Raabe, D., Zhao, X.: Acta Materialia (2013), 61 (12), 4591-4606.
44. Cereceda, D., Diehl, M., Roters, F., Shanthraj, P., Raabe, D., Perlado, J.M., Marian, J.: GAMM Mitteilungen (2015), 38 (2), 213-227.
45. Jia, N., Roters, F., Eisenlohr, P., Kords, C., Raabe, D.: Acta Materialia (2012), 60, 1099-1115.
46. Zheng, C., Raabe, D., Li, D.: Acta Materialia (2012), 60, 4768-4779.
47. Liu, B., Eisenlohr, P., Roters, F., Raabe, D.: Acta Materialia (2012), 60, 5380-5390.
48. Liu, B., Raabe, D., Roters, F., Arsenlis, A.: Acta Materialia (2014), 79, 216-233.
49. Hafez Haghighat, S.M., Schäublin, R., Raabe, D.: Acta Materialia (2014), 64, 24-32.
50. Reuber, C., Eisenlohr, P., Roters, F., Raabe, D.: Acta Materialia (2014), 71, 333-348.

51. Zheng, C., Raabe, D.: Acta Materialia (2013), 61, 5504-5517.
52. Jia, N., Raabe, D., Zhao, X.: Acta Materialia(2014), 76, 238-251.
53. Jia, N., Eisenlohr, P., Roters, F., Raabe, D., Zhao, X.: Acta Materialia (2012), 60, 3415-3434.
54. Wang, F., Sandlöbes, S., Diehl, M., Sharma, L., Roters, F., Raabe, D.: Acta Materialia (2014), 80, 77-93.
55. Roters, F., Eisenlohr, P., Bieler, T.R., Raabe, D.: Crystal Plasticity Finite Element Methods in Materials Science and Engineering. Wiley-VCH, Weinheim (2010).
56. Roters, F., Eisenlohr, P., Hantcherli, L., Tjahjanto, D.D., Bieler, T.R., Raabe, D.: Acta Materialia (2010), 58, 1152-1211.
57. Bieler, T.R., Eisenlohr, P., Roters, F., Kumar, D., Mason, D.E., Crimp, M.A., Raabe, D.: International Journal of Plasticity (2009), 25 (9), 1655-1683.
58. F. Roters, Advanced material models for the crystal plasticity finite element method — development of a general CPFEM framework, Habilitationsschrift RWTH Aachen (2011), Fakultät für Georessourcen und Materialtechnik.
59. P. Eisenlohr, M. Diehl, R.A. Lebensohn, F. Roters: International Journal of Plasticity 46 (2013), 37-53.
60. P. Shanthraj, P. Eisenlohr, M. Diehl, F. Roters: International Journal of Plasticity 66 (2015), 31-45.
61. He, D., Zhu, J.C., Zaefferer, S., Raabe, D., Liu, Y., Lai, Z.L., Yang, X.W.: Materials Science and Engineering (2012) A, 549, 20-29.
62. Mandal, S., Pradeep, K.G., Zaefferer, S., Raabe, D.: Scripta Materialia (2014), 81, 16-19.
63. Sandlöbes, S., Pei, Z., Friák, M., Zhu, L.-F., Wang, F., Zaefferer, S., Raabe, D., Neugebauer, J.: Acta Materialia (2014), 70, 92-104.
64. Schemmann, L., Zaefferer, S., Raabe, D., Friedel, F., Mattissen, D.: Acta Materialia (2015), 95, 386-398.
65. Yuan, L., Ponge, D., Wittig, J., Choi, P., Jiménez, J.A., Raabe, D.: Acta Materialia (2012), 60, 2790-2804.
66. Calcagnotto, M., Ponge, D., Raabe, D.: ISIJ International (2012), 52 (5), 874-883.
67. Raabe, D., Sandlöbes, S., Millán, J., Ponge, D., Assadi, H., Herbig, M., Choi, P.-P.: Acta Materialia (2013), 6, 6132-6152.
68. Nakada, N., Tsuchiyama, T., Takaki, S., Ponge, D., Raabe, D.: ISIJ International (2013), 53 (12), 2275-2277.
69. Millán, J., Sandlöbes, S., Al-Zubi, A., Hickel, T., Choi, P., Neugebauer, J., Ponge, D., Raabe, D.: Acta Materialia (2014), 76, 94-105.
70. Zhang, H., Pradeep, K.G., Mandal, S., Ponge, D., Raabe, D.: Acta Materialia (2014), 80, 296-308.
71. Zhang, H., Pradeep, K.G., Mandal, S., Ponge, D., Choi, P., Tasan, C.C., Raabe, D.: Acta Materialia (2014), 63, 232-244.
72. Wang, M.-M., Tasan, C.C., Ponge, D., Kostka, A., Raabe, D.: Acta Materialia (2014), 79, 268-281.
73. Li, Y.J., Ponge, D., Choi, P., Raabe, D.: Scripta Materialia (2015), 96, 13-16.
74. Dmitrieva, O., Ponge, D., Inden, G., Millán, J., Choi, P., Sietsma, J., Raabe, D.: Acta Materialia (2011), 59, 364-374.
75. Calcagnotto, M., Adachi, Y., Ponge, D., Raabe, D.: Acta Materialia (2011), 59, 658-670.
76. Springer, H., Raabe, D.: Acta Materialia (2012), 60, 4950-4959.
77. Springer, H., Aparicio Fernandez, R., Duarte, M.J., Kostka, A., Raabe, D.: Acta Materialia (2015), 96, 47-56.
78. Reeh, S., Music, D., Gebhardt, T., Kasprzak, M., Jäpel, T., Zaefferer, S., Raabe, D., Richter, S., Schwedt, A., Mayer, J., Wietbrock, B., Hirt, G., Schneider, J.M.: Acta Materialia (2012), 60 (17), 6025-6032.
79. Springer, H., Belde, M., Raabe, D.: Materials Science and Engineering A (2013), 582, 235-244.
80. Springer, H., Szczepaniak, A., Raabe, D.: Acta Materialia (2015), 96, 203-211.
81. Raabe, D., Tasan, C.C., Springer, H., Bausch, M.: Steel Research International (2015), 86 No. 10 1127-1138.
82. Belde, M., Springer, H., Inden, G., Raabe, D.: Acta Materialia (2015), 86, 1-14.
83. Raabe, D., Springer, H., Gutierrez-Urrutia, I., Roters, F., Bausch, M., Seol, J.-B., Koyama, M., Choi, P.-P., Tsuzaki, K.:JOM (2014), 66 (9), 1845-1856.
84. Mehrtens, T., Schowalter, M., Tytko, D., Choi, P., Raabe, D., Hoffmann, L., Jönen, H., Rossow, U., Hangleiter, A., Rosenauer, A.: Journal of Physics: Conference Series (2013), 471 (1), art. no. 012009.
85. Parsa, A.B., Wollgramm, P., Buck, H., Somsen, C., Kostka, A., Povstugar, I., Choi, P.-P., Raabe, D., Dlouhy, A., Müller, J., Spiecker, E., Demtroder, K., Schreuer, J., Neuking, K., Eggeler, G.: Advanced Engineering Materials (2015), 17 (2), 216-230.
86. Li, Y.J., Choi, P., Goto, S., Borchers, C., Raabe, D., Kirchheim, R.: Acta Materialia (2012), 60, 4005-4016.
87. Chen, Y.Z., Herz, A., Li, Y.J., Borchers, C., Choi, P., Raabe, D., Kirchheim, R.: Acta Materialia (2013), 61 (9), 3172-3185.

88. Peng, Z., Povstugar, I., Matuszewski, K., Rettig, R., Singer, R., Kostka, A., Choi, P.-P., Raabe, D.: Scripta Materialia (2015), 101, 44-47.

89. Povstugar, I., Choi, P.-P., Tytko, D., Ahn, J.-P., Raabe, D.: Acta Materialia (2013), 61 (20), 7534-7542.

90. Cojocaru-Mirédin, O., Choi, P., Wuerz, R., Raabe, D.: Applied Physics Letters (2012), 101 (18), art. no. 181603.

91. Schwarz, T., Cojocaru-Mirédin, O., Choi, P.-P., Lämmle, A., Würz, R., Mousel, M., Redinger, A., Siebentritt, S., Botti, S., Raabe, D.: Microscopy and Microanalysis (2014), 20 (3), 394-395.

92. Cojocaru-Mirédin, O., Fu, Y., Kostka, A., Sáez-Araoz, R., Beyer, A., Knaub, N., Volz, K., Fischer, C.-H., Raabe, D.: Progress in Photovoltaics: Research and Applications (2015), 23 (6), 705-716.

93. Schwarz, T., Cojocaru-Mirédin, O., Choi, P., Mousel, M., Redinger, A., Siebentritt, S., Raabe, D.: Applied Physics Letters (2013), 102 (4), art. no. 042101.

94. Jägle, E.A., Choi, P.-P., Van Humbeeck, J., Raabe, D.: Journal of Materials Research (2014), 29 (17), 2072-2079.

95. Ma, D., Grabowski, B., Körmann, F., Neugebauer, J., Raabe, D.: Acta Materialia (2015), 100, 90-97.

96. Ma, D., Friák, M., Von Pezold, J., Neugebauer, J., Raabe, D.: Acta Materialia (2015), 98, 367-376.

97. Hickel, T., Sandlöbes, S., Marceau, R.K.W., Dick, A., Bleskov, I., Neugebauer, J., Raabe, D.: Acta Materialia (2014), 75, 147-155.

98. Ma, D., Friák, M., Von Pezold, J., Raabe, D., Neugebauer, J.: Acta Materialia (2015), 85, 53-66.

99. Pei, Z., Ma, D., Friák, M., Svendsen, B., Raabe, D., Neugebauer, J.: Physical Review B - Condensed Matter and Materials Physics (2015), 92 (6), art. no. 064107.

100. Enax, J., Fabritius, H.-O., Rack, A., Prymak, O., Raabe, D., Epple, M.: Journal of Structural Biology (2013), 184 (2), 155-163.

101. Nikolov, S., Petrov, M., Lymperakis, L., Friák, M., Sachs, C., Fabritius, H.-O., Raabe, D., Neugebauer, J.: Advanced Materials (2010), 22 (4), 519-526.

102. Wu, X., Erbe, A., Raabe, D., Fabritius, H.-O.: Advanced Functional Materials (2013), 23 (29), 3615-3620.

103. Enax, J., Janus, A.M., Raabe, D., Epple, M., Fabritius, H.-O.: Acta Biomaterialia (2014), 10 (9), 3959-3968.

104. Fabritius, H.-O., Karsten, E.S., Balasundaram, K., Hild, S., Huemer, K., Raabe, D.: Zeitschrift für Kristallographie (2012), 227 (11), 766-776.

105. Enax, J., Prymak, O., Raabe, D., Epple, M.: Journal of Structural Biology (2012), 178 (3), 290-299.

106. Friák, M., Zhu, L.-F., Lymperakis, L., Titrian, H., Aydin, U., Janus, A.M., Fabritius, H.-O., Ziegler, A., Nikolov, S., Hemzalová, P., Raabe, D., Neugebauer, J.: Key Engineering Materials (2014), 592-593, 335-341.

107. Zhu, L.-F., Friák, M., Lymperakis, L., Titrian, H., Aydin, U., Janus, A.M., Fabritius, H.-O., Ziegler, A., Nikolov, S., Hemzalová, P., Raabe, D., Neugebauer, J.: Journal of the Mechanical Behavior of Biomedical Materials (2013), 20, 296-304.

108. Lübke, A., Enax, J., Loza, K., Prymak, O., Gaengler, P., Fabritius, H.-O., Raabe, D., Epple, M.: RSC Advances (2015), 5 (76), 61612-61622.

109. Raabe, D., Herbig, M., Sandlöbes, S., Li, Y., Tytko, D., Kuzmina, M., Ponge, D., Choi, P.-P.: Current Opinion in Solid State and Materials Science (2014), 18 (4), 253-261.

110. Tytko, D., Choi, P.-P., Klöwer, J., Kostka, A., Inden, G., Raabe, D.: Acta Materialia (2012), 60, 1731-1740.

111. Duarte, M.J., Klemm, J., Klemm, S.O., Mayrhofer, K.J.J., Stratmann, M., Borodin, S., Romero, A.H., Madinehei, M., Crespo, D., Serrano, J., Gerstl, S.S.A., Choi, P.P., Raabe, D., Renner, F.U.: Science (2013), 341 (6144), 372-376.

112. Duarte, M.J., Kostka, A., Jimenez, J.A., Choi, P., Klemm, J., Crespo, D., Raabe, D., Renner, F.U.: Acta Materialia (2014), 71, 20-30.

113. Woldemedhin, M.T., Raabe, D., Hassel, A.W.: Electrochimica Acta (2012), 82, 324-332.

114. Kim, J.-H., Kim, B.K., Kim, D.-I., Choi, P.-P., Raabe, D., Yi, K.-W.: Corrosion Science (2015), 96, 52-66.

115. Renner, F.U., Ankah, G.N., Bashir, A., Ma, D., Biedermann, P.U., Shrestha, B.R., Nellessen, M., Khorashadizadeh, A., Losada-Pérez, P., Duarte, M.J., Raabe, D., Valtiner, M.: Advanced Materials (2015), 27 (33), 4877-4882.

116. Haley, D., Merzlikin, S.V., Choi, P., Raabe, D.: International Journal of Hydrogen Energy (2014), 39 (23), 12221-12229.

117. Koyama, M., Tasan, C.C., Akiyama, E., Tsuzaki, K., Raabe, D.: Acta Materialia (2014), 70, pp. 174-187.

118. Koyama, M., Springer, H., Merzlikin, S.V., Tsuzaki, K., Akiyama, E., Raabe, D.: International Journal of Hydrogen Energy (2014), 39 (9), 4634-4646.

119. Koyama, M., Akiyama, E., Sawaguchi, T., Raabe, D., Tsuzaki, K.: Scripta Materialia (2012), 66 (7), 459-462.

120. Koyama, M., Akiyama, E., Tsuzaki, K., Raabe, D.: Acta Materialia (2103), 61 (12), 4607-4618.

121. Wang, M., Tasan, C.C., Koyama, M., Ponge, D., Raabe, D.: Metallurgical and Materials Transactions A (2015), 46 (9), 3797-3802.

122. Kim, J.-K., Sandlöbes, S., Raabe, D.: Acta Materialia (2015), 82, 414-423.

123. Pierce, D.T., Jiménez, J.A., Bentley, J., Raabe, D., Wittig, J.E.: Acta Materialia (2015), 100, 178-190.

124. Gutierrez-Urrutia, I., Raabe, D.: Materials Science and Technology (United Kingdom) (2014), 30 (9), 1099-1104.

125. Plancher, E., Tasan, C.C., Sandloebes, S., Raabe, D. On dislocation involvement in Ti-Nb gum metal plasticity (2013) Scripta Materialia, 68 (10), pp. 805-808.

126. Gutierrez-Urrutia, I., Raabe, D.: Scripta Materialia (2013), 68 (6), 343-347.

127. Pierce, D.T., Jiménez, J.A., Bentley, J., Raabe, D., Oskay, C., Wittig, J.E.: Acta Materialia (2014), 68, 238-253.

128. Toji, Y., Matsuda, H., Herbig, M., Choi, P.-P., Raabe, D.: Acta Materialia (2014), 65, 215-228.

129. Choi, W.S., De Cooman, B.C., Sandlöbes, S., Raabe, D.: Acta Materialia (2015), 98, 391-404.

130. Shen, Y.F., Jia, N., Wang, Y.D., Sun, X., Zuo, L., Raabe, D.: Acta Materialia (2015), 97, 305-315.

131. Pradeep, K.G., Herzer, G., Choi, P., Raabe, D.: Acta Materialia (2014), 68, 295-309.

132. Tarzimoghadam, Z., Sandlöbes, S., Pradeep, K.G., Raabe, D.: Acta Materialia (2015), 97, 291-304.

133. Zhang, J.-L., Tasan, C.C., Lai, M.L., Zhang, J., Raabe, D.: Journal of Materials Science(2015), 50 (17), 15

134. Sandlöbes, S., Friák, M., Zaefferer, S., Dick, A., Yi, S., Letzig, D., Pei, Z., Zhu, L.-F., Neugebauer, J., Raabe, D.: Acta Materialia (2012), 60, 3011-3021.

135. Pei, Z., Zhu, L.-F., Friák, M., Sandlöbes, S., Von Pezold, J., Sheng, H.W., Race, C.P., Zaefferer, S., Svendsen, B., Raabe, D., Neugebauer, J.: New Journal of Physics (2013), 15, art. no. 043020.

136. Nematollahi, G.A., Von Pezold, J., Neugebauer, J., Raabe, D.: Acta Materialia (2013), 61 (5), 1773-1784.

137. Sandlöbes, S., Friák, M., Neugebauer, J., Raabe, D.: Materials Science and Engineering A (2013), 576, 61-68.

138. Friák, M., Counts, W.A., Ma, D., Sander, B., Holec, D., Raabe, D., Neugebauer, J.: Materials (2012), 5 (10), 1853-1872.

139. Pradeep, K.G., Wanderka, N., Choi, P., Banhart, J., Murty, B.S., Raabe, D.: Acta Materialia (2013), 61 (12), 4696-4706.

140. Tasan, C.C., Deng, Y., Pradeep, K.G., Yao, M.J., Springer, H., Raabe, D.: JOM (2014), 66 (10), 1993-2001.

141. Yao, M.J., Pradeep, K.G., Tasan, C.C., Raabe, D.: Scripta Materialia (2014), 72-73, 5-8.

142. Pradeep, K.G., Tasan, C.C., Yao, M.J., Deng, Y., Springer, H., Raabe, D.: Materials Science and Engineering A (2015), 648, 183-192.

143. Ma, D., Yao, M., Pradeep, K.G., Tasan, C.C., Springer, H., Raabe, D.: Acta Materialia (2015), 98, 288-296.

144. Deng, Y., Tasan, C.C., Pradeep, K.G., Springer, H., Kostka, A., Raabe, D.: Acta Materialia (2015), 94, 124-133.

145. Wang, M.-M., Tasan, C.C., Ponge, D., Dippel, A.-Ch., Raabe, D.: Acta Materialia (2015), 85, 216-228.

146. Tytko, D., Choi, P.-P., Raabe, D.: Acta Materialia (2015), 85, 32-41.

147. Friák, M., Tytko, D., Holec, D., Choi, P.-P., Eisenlohr, P. Raabe, D. Neugebauer J.: Synergy of atom-probe structural data and quantum-mechanical calculations in a theory-guided design of extreme-stiffness superlattices containing metastable phases, New J. Phys. 17 (2015) 093004 .

Research Projects in Progress

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

Cojocaru-Mirédin, Raabe: NanoMatFutur - Optimierung des Wirkungsgrades von Solarzellen basierend auf 3-dimensionalen chemischen Analysen auf atomarer Skala (in collaboration with RWTH Aachen)

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

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

Ponge, Springer, Raabe: Bladestrip - Innovative Werkstoffgeneration für Schneidwaren durch die revolutionäre Fertigungstechnologie Bandgießen

Raabe, Schneider, Dehm, Köhler, Schnabel: Topological Engineering of Ultra-Strong Glasses

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

Sandlöbes, Nellessen: Constitutive modelling and microstructural validation for crystal plasticity finite element computation of cyclic plasticity in fatigue (in collaboration with RWTH Aachen)

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

Zaefferer, Raabe: Local texture analysis and crystalline anisotropy in Mn-steels

Sandlöbes, Ponge: Synthesis and Characterization of Fe-Mn reference materials

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

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

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

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

Tarzimoghadam, Ponge: Hydrogen embrittlement in Ni alloys

Wong, Roters: Constitutive modeling of joint TRIP and TWIP deformation of in advanced high strength steels

Zaefferer, Ram: High resolution scanning electron back scatter diffraction experiments and local strain determination in Mn-based steels

Springer, Belde, Baron: Synthesis, alloy design and phase boundary mechanics in multiphase steels

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

Tasan, Diehl, Roters: Simulation of the mechanical response of stable dual phase steels

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

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

Varnik, Raabe: Theoretical investigations on shear bands in colloidal glasses

Department of Structure and Nano-/Micromechanics of Materials

G. Dehm

Scientific Mission and Concepts

The objective of the newly formed department (October 2012) is to perform basic research on microstructure physics and mechanical properties of structural and functional materials with a focus on small length scales down to atomic dimensions. Our mission is to develop and enhance accurate and quantitative *in situ* nano-/micromechanical test methods with the aim to improve and tailor the mechanical properties of materials by resolving the interplay between microstructure components (e.g. phases, interfaces, dislocations) and the resulting mechanical performance (e.g. strength, ductility, toughness). The materials portfolio which we study comprises alloys, in particular steel and intermetallics, and nanocrystalline materials for structural applications as well as thin films for functional applications (e.g. coatings, flexible electronics, semiconductor devices). The aim of our scientific work is to gain fundamental knowledge on plasticity mechanisms with high spatial resolution, as this provides new insights into deformation phenomena, mechanisms of damage accumulation, and finally crack initiation followed by materials failure, and to use this knowledge to develop design criteria to make materials more robust and reliable. The mechanical techniques we apply range from self-designed micro- and nanomechanical test methods to nanoindentation and nanotribological tests. As a prerequisite, a detailed understanding of the microstructure is required. This is accomplished by applying scale bridging characterization techniques such as X-ray diffraction (XRD) and synchrotron methods as well as scanning electron microscopy (SEM) and advanced scanning/ transmission electron microscopy (S/TEM) methods. Our specialty is to combine both approaches – advanced microstructure characterization and localized mechanical testing – permitting to study the evolution of reversible and irreversible deformation processes "live" during the external stimulus.

The department consists of 5 scientific research groups (see Fig. 1) which closely interact amongst each other and within the institute to contribute to MPIE's interdisciplinary mission of developing new high-performance materials for use as high-tech structural and functional components. In addition, the research groups also pursue their own scientific agenda to tackle central scientific questions within their research themes. Currently, the department has 4 groups in operation: Dr. Christian Liebscher was attracted from University of California at Berkeley as head of the Advanced Transmission Electron Microscopy group (since April 2015, see p. 27), Dr. Steffen Brinckmann from the Ruhr-Universität Bochum as head of the Nanotribology group (since December 2014, see p. 22), and Dr. Christoph Kirchlechner form the Montanuniversität Leoben (Austria) leads since March 2013 the group Nano-/ Micromechanics of Materials (see p. 26), which

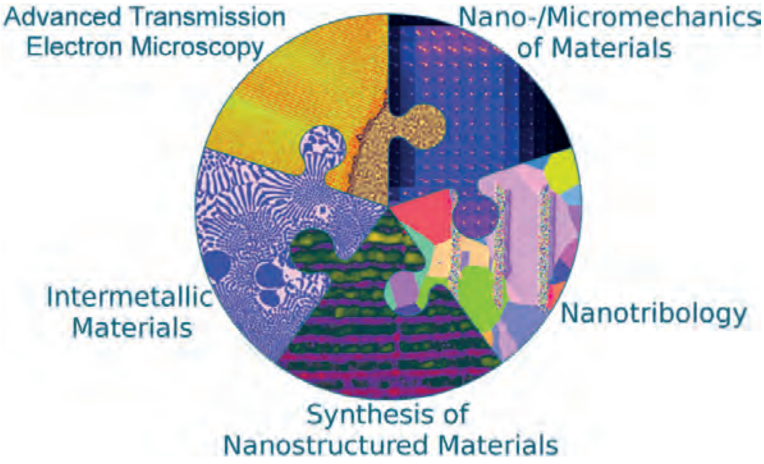


Fig. 1: *Interacting groups of the SN department.*

also includes the XRD and synchrotron activities of the department. The research group Intermetallic Materials was until September 2012 temporarily allocated to the MA-Department (Microstructure Physics and Alloy Design) and transferred with October 2012 into the newly formed SN-Department and is co-headed by Dr. Martin Palm and Dr. Frank Stein. The 5th research group, which will deal with the Synthesis of Nanostructured Materials, will be advanced when the reconstruction work of hall 8/9 and the installation of the new facilities have been finished.

Since its foundation in fall 2012 the SN-Department consequently focused on installing and operating the newly required experimental infrastructure and expedited the necessary reconstruction of hall 8/9 to host the institutes advanced S/TEM facility and a laboratory for TEM sample preparation. The new equipment includes a focused ion beam work station (FIB), a commercial *in situ* mechanical testing platform installed inside the SEM, a self-made nano-/micromechanical test rig, which is mainly dedicated for µLaue synchrotron diffraction experiments, a nanoindenter system with lateral force sensor for quantitative nanotribological measurements combined with a home-build electrochemical cell. The latter system will allow in future studying the mechanical and tribological behaviour of materials under environmental conditions - synergistically with the GO-Department (Interface Chemistry and Surface Engineering). "Live" observation of microstructural changes caused by external stimulus can be probed with dedicated TEM holders (liquid cell, indentation, and a heating holder) opening a window into the nanometer length scale of materials phenomena in corrosion science, mechanical properties, and thermodynamics. Last but not least, an aberration corrected S/TEM for structural and analytical microstructure characterization at the atomic level went into scientific operation in July 2015. The new advanced S/TEM equipment complements MPIE's advanced characterization infrastructure, especially the 3-dimensional atom probe tomography (APT) facilities (MA-Department) with its unprecedented chemical sensitivity, by permitting atomic resolved structure and bonding analyses of phases, interfaces and other microstructural components of high performance materials.

Although the start of a number of new facilities within a short period of time is a challenge by itself, several major scientific achievements have been accomplished by our research in the last 3 years. In the field of Nano-/ Micromechanics of Materials we have made significant progress in performing accurate miniaturized fracture mechanics tests. The lack of standards necessitates determining the accuracy and limits of the applied testing techniques. We used silicon as a well-known reference material to benchmark 4 different miniaturized fracture testing schemes [1]. Based on the findings we were able to expand the methodology to metallic glasses in form of thin films to uncover the origin of brittleness and ductility of such materials [2] within an interdisciplinary cooperation including the MA-Department and the RWTH Aachen with the recently founded Max Planck Fellow Group Self Reporting Materials headed by Professor Jochen Schneider.

Our advanced synchrotron experiments on heavily wire drawn pearlitic steel uncovered an unexpected phase transformation from ferrite to martensite as a consequence of the decomposition process of the cementite phase. Dr. Soundes Djaziri and Dr. Christoph Kirchlechner discovered by an in-depth analysis of the diffraction data concerning texture, internal strain, and lattice parameters of pearlitic wires, that for wires exposed to drawing strains exceeding 200% the ferrite lattice becomes tetragonally distorted. The close collaboration with the departments MA and CM (Computational Materials Design) led to a profound understanding of the origin of the transformation and to the conclusion that the tetragonal ferrite indeed corresponds to a strain induced martensite. APT measurements revealed that the carbon content inside the ferrite grains exceeded the solubility limit, which at a certain concentration level leads to a spontaneous carbon ordering at specific octahedral sites of the bcc lattice, as found out by computational modelling performed by the CM-Department. This corresponds to the carbon ordering in martensite created by quenching austenite. Thus, the decomposition of cementite in the pearlite wires causes a carbon supersaturation of ferrite, which in turn leads to the strain-induced martensite formation – a new mechanisms which was previously overlooked.

The interplay between microstructure physics and mechanical properties is also at the core of our studies on interface plasticity and fracture [3-13]. As an example, dislocation transmission across twin boundaries was revisited by *in situ* and *post mortem* µLaue diffraction, SEM and S/TEM imaging – always combined with quantitative global stress and strain measurements. All our experiments revealed that the coherent Σ3(111) Cu twin boundary exerted no measurable increase in strength compared to single crystals of the same size and orientation, a result opposing molecular dynamic predictions in the literature which claim that shear stresses of more than 400 MPa are required for dislocation transmission.

Grain boundaries intersected by scratches permit in nanotribology to study dislocation transmission, absorption, nucleation or pile-ups at interfaces by analyzing the slip markings on the surface and changes in grain orientation by electron backscatter

Fig. 2: *Members of the SN department (picture taken in Sep. 2015).*

diffraction (EBSD) in the SEM [14,15]. Also in thin film systems like metal films on polymers the interface is detrimental for the film adhesion and mechanics. We studied the influence of Cr adhesion layers for Cu films on polyimide substrates and found out that although the Cr layer promotes adhesion it significantly deteriorates the resistance of the Cu against failure by cracking. Channel cracks forming in the brittle adhesion layer lead to significant stress concentrations in the adjacent Cu film causing failure at much lower strains than for Cu films directly applied to the polyimide substrate [16,17]. This finding has significant influences for flexible electronic devices.

The new department is already well connected within MPIE and has also established contacts to the Ruhr Universität Bochum (RUB), where G. Dehm is associated at the Materials Research Department and the Institute for Materials (Institut für Werkstoffe) as a professor (Außerplanmäßiger Professor). The SN-Department hosts the research group High Temperature Materials headed by Prof. Gunther Eggeler, which continues the previously established Max Planck Fellow Group that expired in the beginning of 2015 after completion of its 5-year funding period. Interactions with Prof. Alfred Ludwig (RUB) within the International Max Planck Research School for Surface and Interface Engineering in Advanced Materials (IMPRS-SurMat) on combinatorial thin film Cu alloy design for energy systems, Prof. Jochen Schneider (RWTH Aachen) on hard coatings and metallic glasses, as well as Prof. Mick Feuerbacher (Jülich) and Prof. Easo George (RUB) on high entropy alloys have been realized. The department also started to interact with steel companies and was host for two 1 year secondments of industry researchers on Precipitate characterization in electrical steels and on Nanomechanics of steel. In addition, we are active in acquiring third party funds such as the EPPL-project (Enhanced Power Pilot Line) funded within the ENIAC Joint Undertaking to strengthen Europe's leading position in power semiconductors, DFG projects on µLaue investigations of dislocation-grain boundary interactions (Dr. C. Kirchlechner) and on novel Fe-Al alloys with fine-scaled lamellar microstructures (Dr. F. Stein), and a collaboration with 5 European industrial partners (HERCULES-2) within the framework of Horizon 2020 on Intermetallics for engine applications (Dr. M. Palm).

The SN-Department holds regularly seminars where the students, postdocs and senior scientists report on their current research topics, and once a year a department retreat jointly with the independent research group Nanoanalytics and Interfaces (Prof. Christina Scheu) and external scientists is performed to discuss the individual research topics and to strengthen interactions within the department. Joint interdepartmental seminars on topics of relevance for more than one department provide the major platform for in-house collaborations on specific strategic topics. Additionally, workshops and conferences are organized by SN-Department members to foster international collaborations and exchanges. Examples are the Mecano General Meeting „Mechanics of Nano-Objects“ (18 - 19 July 2013) at MPIE organized by G. Dehm, the workshop on “Bridging the scales in tribology and wear” jointly organized by S. Brinckmann and M. Valtiner (GO-Department), the conference “Intermetallics” 2013 and 2015 (30 September - 4 October 2013 and 28 September - 02 October 2015, Kloster Banz) co-organized by F. Stein and M. Palm, the Symposium “Structure and dynamics V: Mechanical properties at small scales” at Condensed Matter CMD25-JMC14 (24 - 29 August, Paris, France) co-organized by G. Dehm, the “Intermetallics“ Technical Committee Meetings of the German Society for Metals (DGM) at the Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, 10 Jan. 2013, and at MPIE, Düsseldorf, 26 Feb. 2014, both organized and chaired by M. Palm, who also was head of this committee until 2014, and the workshop on “Rasterkraftmikroskopie und nanomechanische Methoden” co-organized by C. Kirchlechner (held at MPIE 27 - 28 Feb. 2014 and in Darmstadt on 5 - 6 Mar. 2015), who became recently head of this technical committee of the DGM.

The success of the scientific work of the members of the SN-Department is reflected by numerous invitations to lectures at conferences and university/institute colloquia. Prestigious examples include two invited talks from C. Kirchlechner and G. Dehm at the Gordon Research Conference on Thin Film & Small Scale Mechanical Behavior (2014), an invited talk by C. Kirchlechner at the ECI conference Nanomechanical Testing in Materials Research and Development V (2015), and invited talks at Fall MRS meetings (2013, 2014, 2015) by C. Kirchlechner and G. Dehm. In 2015, B.N. Jaya presented invited talks at the International Conference on Metallurgical Coatings and Thin Films (ICMCTF 2015) and the 17th International Conference on the Strength of Materials (ICSMA 17), and G. Dehm gave an invited talk at the Frontier of Electron Microscopy in Materials Science (FEMMS 2015) and a keynote lecture at EUROMAT 2015.

We also promote career opportunities for the young scientists in industry and launched a new series at MPIE jointly with the MPIE PhD representatives called Career Talks. The first career talk took place on 27th of March with the ThyssenKrupp Steel Europe AG explaining their job portfolio followed by a get-together, where in an informal atmosphere contacts were exchanged. This was followed by an onsite visit at ThyssenKrupp Steel Europe AG in Dortmund on 4th of May 2015. Due to the positive response of all involved parties, 2-3 career talks per year with further industrial partners are planned. The next ones are with McKinsey and Company in October 2015 and with BASF in November 2015 (see p. 58).

In the following, the research activities of the research groups of the SN-Department are provided and selected projects summarized.

Scientific Groups

Nano- and Micromechanics of Materials (C. Kirchlechner)

The Nano- and Micromechanics Group - More than a mechanical microscope. Advances in micro sample preparation, micromechanical testing and nondestructive microstructural characterization enable us today to explore the mechanical behaviour at hitherto unreached small dimensions. Aim of our research is to study the mechanical behaviour of materials at the microstructural length scale. Our work is stimulated by various questions in advanced material science, such as (i) the origin of size-dependent mechanical behaviour of single crystals, (ii) the quantitative understanding of individual deformation mechanisms governing plasticity in complex microstructures, (iii) the quantification of damage accumulation in individual microstructural constituents during cyclic loading and, finally, (iv) the micro fracture behaviour of phases and interfaces.

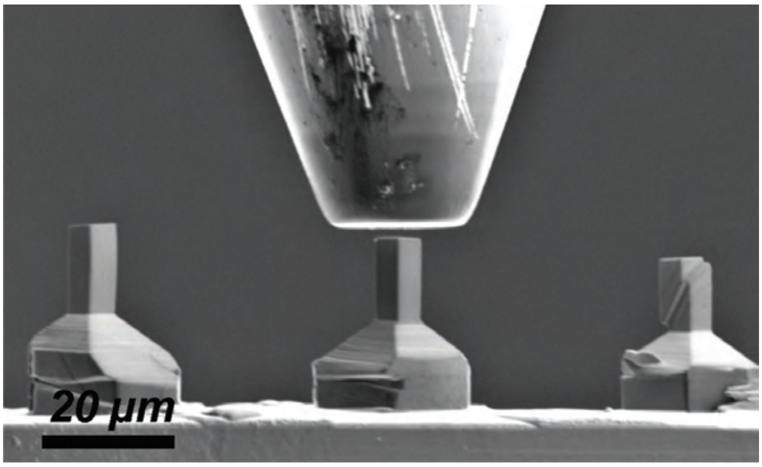


Fig. 3: *SEM images of single and bi-crystalline copper micropillars. The two outer pillars are single crystalline references, the centered one being ready for loading by the indenter is bi-crystalline.*

The intended purpose surpasses measuring local mechanical properties by far. A central aspect of our work is to interlink the underlying and evolving defect structures (e.g. dislocation types and densities, length and density of cracks and crack networks, etc.) with the mechanical response. This requires advanced characterization methods and dedicated *in situ* equipment, which are both developed in house.

Buildup of micromechanical capabilities. After the group was found in spring 2013, the main focus was put on the buildup of *in situ* micromechanical capabilities (see p. 30). Micro loading rigs for *in situ* SEM and *in situ* µLaue diffraction (SSD2) performed at the European Synchrotron Radiation Facility (ESRF), as well as a focus ion beam system (Zeiss Auriga®, Zeiss Oberkochen) were successfully implemented in 2013. Characteristic sample dimensions of these machines are ranging from hundreds of nanometer to tens of micrometers. The aforementioned methods permit deep insights into the cumulative behaviour of dislocations during mechanical loading and therefore are of central importance for our group. Complementary, mid 2014 we successfully implemented a Hysitron PI-95 PicoIndenter® being able to perform *in situ* TEM, which gives us a detailed view on individual dislocations and their interaction with other lattice defects. Our today's equipment is well able to measure important microstructural parameters during *in situ* deformation. Examples are monitoring sample shape changes (*in situ* SEM), deviatoric strains and strain gradients as well as the cumulative behaviour of geometrically necessary dislocations (*in situ* µLaue) and the interaction of individual dislocations with other defects (*in situ* TEM). The complementary characterization methods span over the most important hierarchical levels in structural materials, which is prerequisite to formulate mechanisms-based material laws.

Size-dependent crystal plasticity. The size dependence of single crystals had been investigated during the last decade. Even though not formulated as a mechanism based material model, the importance of dislocation source sizes and source availability is well known and suggested by several studies. Remaining questions in this field are the impact of elevated temperatures on the size dependent behaviour, as well as the size scaling of non-cubic crystal structures. As one research highlight we aim for understanding of the size dependent material properties in tetragonal body centered tin. Particularly interesting in this material – being in our focus due to the demand of lead free solder joints of the automotive electronic industries – is that the operating slip systems are yet unknown, and that our experiments can be conducted at very high homologous temperatures of 0.6. The main results are (i) that hardly any dislocations are stored during deformation, (ii) that the size scaling exponent is close to a theoretical value of -1 and finally, (iii) that slip is highly anisotropic with different slip systems being operated in different crystallographic loading directions [18].

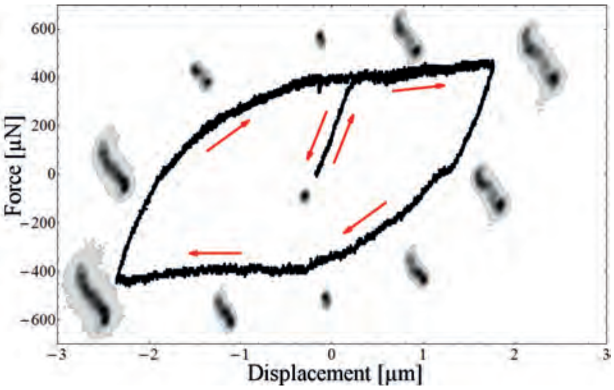


Fig. 4: *Cyclic force displacement curve of a micron-sized, single crystalline bending cantilever with superimposed Laue images. Initially, the Laue spot is circular documenting the lack of geometrically necessary dislocations (GNDs). During beam deflection, GNDs are stored and are forming subgrains within the probed volume. Interestingly, backbending leads to significant reduction of the stored GNDs with negligible GND content in straight beams [19].*

Grain-boundary dislocation interaction mechanisms. Another research highlight and one of the main objectives of the group is to understand grain-boundary (GB) dislocation interaction mechanisms. For this purpose, bi-crystals with specific grain-boundaries are grown by a Bridgman furnace or extracted from well-recrystallized polycrystals. Currently we focus on Cu as a model material. Miniaturized compression (see Fig. 3) and tensile samples with sizes ranging from 500 nm up to 15 µm are produced by FIB milling. During *in situ* testing the piling up of dislocations at the GB, their annihilation at the GB as well as the slip transfer of dislocations through the GB into the next grain are quantified. It is our aim to understand the GB-dislocation interaction in a broad context: various grain boundary types, e.g. coherent Σ3 (111) twins, general large angle grain-boundaries allowing for slip transfer or being strong obstacle for dislocation transfer, and small angle tilt grain-boundaries are tested. In case of the coherent Σ3 (111) twin loaded in <110> we observed dove-tail shaped slip lines where dislocations cross-slipped from one into the second grain. Surprisingly, the slip transfer mechanism does not have any impact on the mechanical behaviour of the twin boundary compared to the single crystalline references [4]. Furthermore, no pronounced pile-up was observed during *in situ* TEM [7] and µLaue diffraction experiments, which suggests that the cross-slip of dislocations through the twin-boundary is not strength dominating at this size regime.

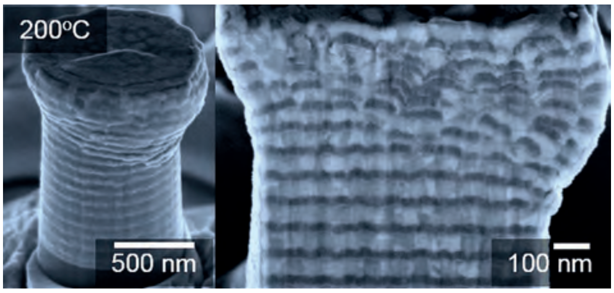


Fig. 5: *Nano-laminated pillar with 66 nm Cu // 33 nm Cr after deforming it to roughly 20% engineering strain (left: full pillar; right: cross-section) [21].*

Besides monotonic loading, structural components have to withstand cyclic loading during service. During the past years we have implemented micro-fatigue experiments on single crystalline micro-bending beams [19] and polycrystalline microsamples [20] to study the impact of cyclic strain gradients as well as the role of a limited number of grain-boundaries on the cyclic behaviour of materials. In the single crystalline bending beams, an almost full reversibility of dislocation multiplication and annihilation can be observed for special sample orientations. This can be seen by the fully reversible peak broadening presented in Fig. 4. However, the reversibility is strongly dependent on the character of dislocation pile-ups. Thus, the geometric orientation of interfaces with respect to the slip systems defines if fatigue damage accumulates or not.

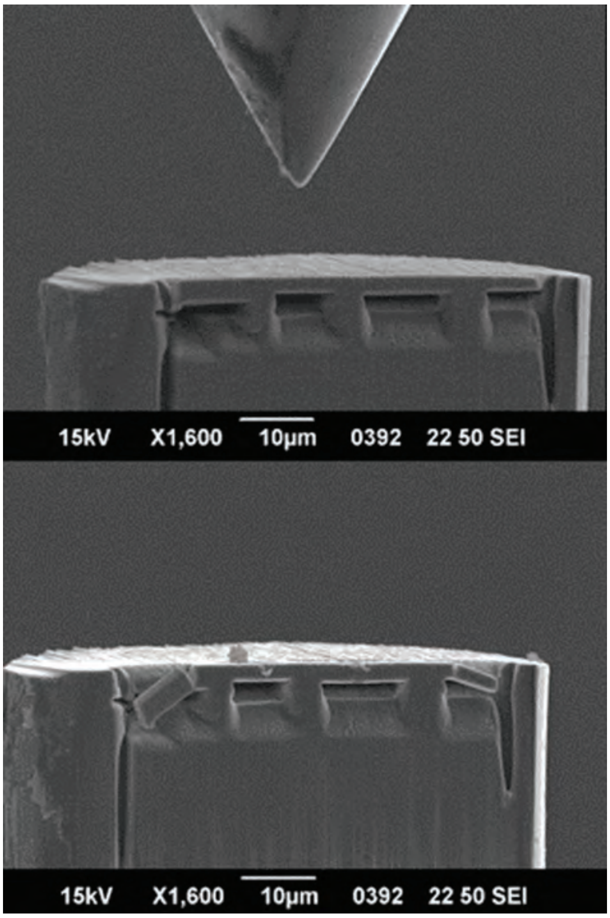


Fig. 6: *Micro-fracture cantilevers milled into a drawn pearlitic steel wire before (top) and after (bottom) fracture experiments.*

Small-scale mechanical behaviour of complex microstructures. Superior performance with multiple different loading and application scenarios (e.g. simultaneous exposure to load and temperature, load and radiation, or current and heat) require complex microstructures. Nano-laminated thin films are a promising candidate, but thorough phenomenon based knowledge is still lacking. To gain deeper insight Cu-Cr thin films with individual layer thicknesses less than 100 nm had been deposited by molecular beam epitaxy. The systems had been analyzed by advanced TEM techniques (SN-Department, Advanced Transmission Electron Microscopy group) and deformed at temperatures up to 300 °C, whereas the high temperature experiments had been performed in collaboration with the EMPA (Swiss Federal Laboratories for Materials Science and Technology) in Thun, Switzerland. An example of a deformed micro specimen is presented in Fig. 5. One of our findings was that the strength surpasses values as predicted by the confined layer slip model or Hall-Petch strengthening [21].

Fracture mechanics at the micron scale. Down-scaling standard fracture mechanical experiments to the micron scale is not straight forward: The size of the plastic zone with respect to the sample size, the impact of friction and the ability to perform geometrically well-defined loading experiments had been questioned ever-since the first micro-fracture mechanical experiments had been shown. This problem gets more and more relevant since various different loading geometries had been proposed. Consequently, the first step within the Nano-/Micromechanics of Materials group was to compare results of available micro-fracture geometries to the known fracture toughness of bulk silicon [1]. Main and surprising outcome of this study is, that – if the plastic zone size is of negligible size and the experiment is performed in a geometrically well-defined way – all tested geometries yield comparable and within the experimental scatter accurate fracture toughness values (between 0.75 and 0.89 MPam$^{1/2}$). But still, milling time, sensitivity to misalignments and experimental errors, as well as the machine performance important for stable crack growth favors one over the other approach.

Since that proof of principals several projects within the MPIE and with international collaborators had been started to explore the fracture toughness of metallic glasses (MA-Department and RWTH Aachen, Germany, see p. 143), of Si and SiO_2 at non-ambient temperatures (EMPA, Thun, Switzerland)

and of multilayered hard-coatings (TU Wien, Austria). Also the fracture toughness of drawn pearlitic steels wires, as shown in Fig. 6 had been explored. At low drawing strains (<3) the assumption under linear elastic fracture mechanics are invalid and we are currently not able to provide J_{IC} measurements in these systems. However, drawing makes the wire increasingly brittle plateauing at roughly 10 $MPam^{1/2}$. Interestingly, the drop in fracture toughness goes hand in hand with an observed tetragonalization of the ferritic iron and a supersaturation of carbon (MA-Department), which had been proofed by our dedicated monochromatic synchrotron experiments and atomistic simulations (CM-Department) [22].

Adhesion properties of metallic thin films on compliant substrates. Besides studying the mechanical response of FIB-milled samples, also approaches to study plasticity and fracture of thin films had been conducted. Examples are the role of an adhesion promoting chromium interlayer on the mechanical performance of a copper layer [17]. Therefore, three film thicknesses (50,100 and 200 nm) were deposited with and without a 10 nm chromium layer on polyimide. Synchrotron-based powder diffraction applying the $\sin^2\psi$ method was used to measure the (copper) film stresses in longitudinal as well as transversal direction during tensile testing. At low strains all films follow the smaller-is-stronger trend, thus being well within our expectations. However, in the film systems with adhesion promoting chromium layer the film stresses rapidly drop at low strains. In all cases this was caused by the mechanical failure of the brittle chromium interlayer. In the thinner copper films (50 nm and 100 nm thick) the copper was not able to prevent through channel cracks as presented in Fig. 7 leading to a total electrical failure of the film systems. In contrast, the 200 nm film was able to stop crack propagation to a certain extend and thus, its behaviour does not significantly differ from the films without adhesion promoting interlayer. Our experimental findings had been supported by cohesive zone modelling performed by the groups of Prof. Rammerstorfer (TU Wien, Austria) and Prof. Fischer (Montanuniversität Leoben, Austria). Similar experiments are currently under way to explore the ability of phase transformations in a cobalt based system to act as failure preventing mechanism.

Outlook. In the future, our now well established setup will be applied for several advanced questions in materials science across the SN-Department and other research groups from the MPIE. Examples are (i) a continuation of investigating the dislocation grain boundary interaction mechanisms and its impact on fatigue at the micron scale (ii) the mechanical behaviour of multilayered film systems with designed interfaces (iii) the ability of phase transformations to enhance fracture properties at the micron scale and (iv) finally, implementing high temperature capabilities.

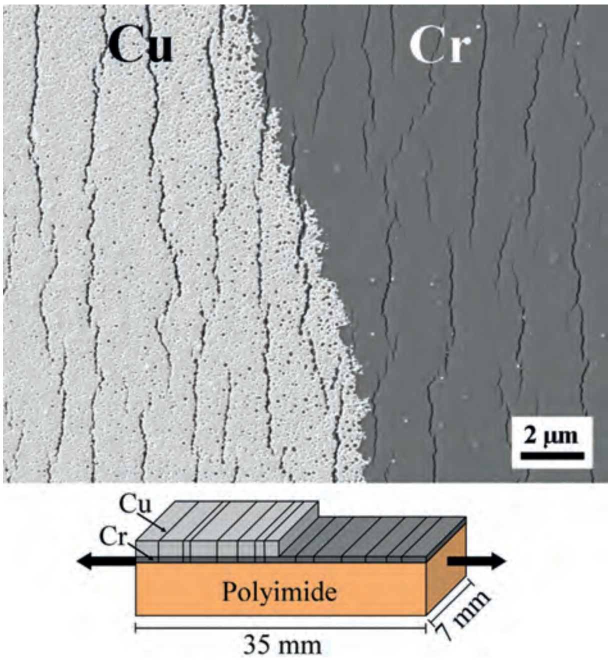


Fig. 7: *Crack network in a thin film system consisting of a polyimide substrate with 10 nm chromium interlayer and 50 nm copper layer as published in [17].*

Advanced Transmission Electron Microscopy (C. Liebscher)

Introduction and mission.

The research of the newly established group Advanced Transmission Electron Microscopy revolves around the application and development of advanced TEM techniques to investigate structural and functional materials from the atomic level up to mesoscopic length scale. We are specifically interested in understanding the atomistic and chemical structure of solid-state defects and interfaces in materials and their behaviour and interaction observed under *in situ* conditions. This fundamental knowledge serves as a solid comparison for atomistic predictions (e.g. by the CM-Department) and is used to develop materials design strategies tailoring desired properties by manipulating materials on the atomic scale. Advanced TEM offers the essential techniques to investigate and manipulate materials on this length-scale bridging approach. Aberration-corrected electron microscopy enables the structural characterization of materials with atomic resolution containing all necessary information about crystallography, chemistry and electronic structure of defects, interfacial phenomena and precipitate structures. In combination with *in situ* techniques the structure and properties are sampled simultaneously closing the missing link between microstructure and properties.

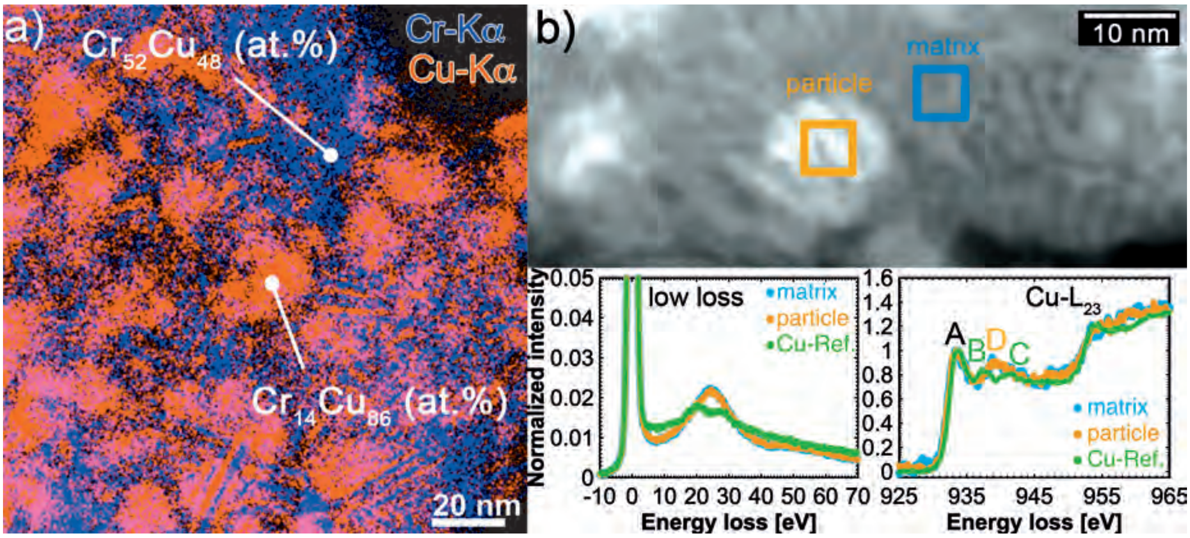


Fig. 8: *a) STEM-EDS elemental maps of an as-deposited $Cu_{66}Cr_{34}$ sample. The microstructure is decomposed into Cr-rich (matrix) and Cu-rich (particle) regions. b) HAADF-STEM image and corresponding low and core loss spectra acquired with dual channel EELS. The spectra are compared to a pure fcc-Cu reference sample. The Cu-L_{23} edge of fcc-Cu shows 2 distinct peaks B and C after the L_3-edge (A). The near edge fine structure for bcc-type Cu exhibits only one peak D after the L_3-edge due to a difference in bonding characteristics.*

Facilities. The group utilizes three TEMs. A FEI/Phillips CM20 with LaB_6 emitter is used for conventional diffraction contrast imaging and electron diffraction experiments. A JEOL JEM2200FS with Schottky field emitter and in-column omega energy-filter enables the characterization of materials with lattice resolution. In addition, the JEM2200FS is the main platform for *in situ* TEM experiments with three available third party *in situ* solutions:

- in situ heating experiments with nanometer resolution are performed with a MEMS-based (Micro-Electro-Mechanical-Systems) DENSsolutions double-tilt heating holder allowing temperatures up to 1200 ºC.
- The nano-mechanical properties and related deformation behaviour are probed with a Hysitron PI 95 PicoIndenter (force resolution of ~200 nN and displacement resolution of ~1 nm).
- The real-time behaviour of materials in liquid electrochemical environment is studied in a Protochips Poseidon 210 holder in cooperation with the GO-Department (Dr. K. Mayrhofer and Dr. N. Hodnik).

A probe-corrected FEI Titan Themis is commissioned and fully operational since July 2015. Through its C_s-probe corrector, the microscope is mainly dedicated for atomic resolution scanning TEM (STEM) enabling a resolution down to 0.07 nm. The microscope combines a monochromated, high-brightness electron gun with a C_s-probe corrector and high-resolution energy-dispersive X-ray spectroscopy (EDS) detectors and an electron energy-loss spectroscopy (EELS) detector (see p. 32). The TEM facilities are complemented by the arrival of an image-side corrected FEI Titan Themis estimated for mid 2016.

Although the new group leader started at 1st of April 2015, several research projects within the themes of the Advanced TEM group had been started previously and selected examples are described below.

Structure and stability of nanocrystalline alloys. In a current project, we analyze the phase stability and segregation behaviour of super-saturated solid solutions of fcc Cu and bcc Cr. Exceeding the solubility limit and “stabilizing” grain boundaries by segregation is a novel route to obtain nanocrystalline grain sizes and prevent rapid coarsening during thermal exposure. For the system Cu-Cr the mutual equilibrium solubility is below 0.8at%. However, by co-deposition of both elements we managed to obtain single phase bcc thin films consisting of extremely high Cu concentrations (e.g. 66at%Cu34at%Cr) as proofed by electron diffraction and analytical TEM [23]. The electronic structure of the Cu L_{23} edge of the bcc structure reveals differences compared to fcc Cu and is under further investigation by us in cooperation with Dr. C. Freysoldt (CM-Department), as illustrated in Fig. 8. A super-saturated fcc CuCr alloy can be obtained up to 4 at.% Cr and remains fcc at temperatures of 300°C. At temperatures of 400 to 500°C film decomposition takes place via nucleation and growth of Cr precipitates. In addition, the *in situ* TEM experiments permitted to determine the Cr diffusion coefficient and an apparent activation energy of 157±4 kJ mol^{-1} indicating grain boundary diffusion as the predominant diffusion path [24].

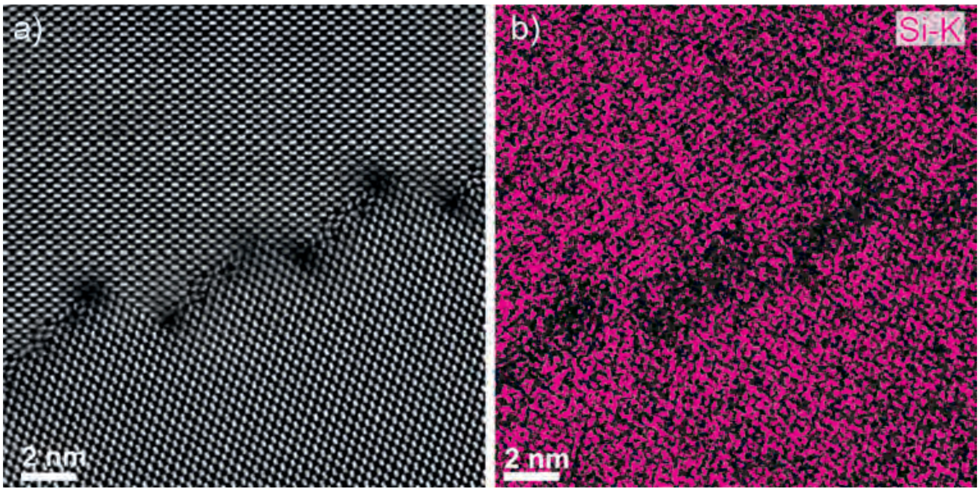


Fig. 9: *a) HAADF-STEM image of a ∑ 3{112} grain boundary extracted from an intentionally doped multicrystalline silicon wafer. Faceting and structural variations along the grain boundary are clearly resolved. b) Lattice fringes from the Si grains are observed in the STEM-EDS elemental map of Si. The Si EDS-signal decreases in certain regions along the grain boundary indicating a lower occupancy of the Si atomic columns. The samples are provided within a collaborative project with A. Stoffers and Dr. O. Cojocaru-Mirédin of the MA-Department.*

Peculiarities of metal-oxide interfaces. Of central interest in our research are interfaces, especially between dissimilar material classes as this is technologically relevant (hard coatings on metals, oxide layers on metals, metallization layers on polymers or insulators), but also scientifically rewarding as interfaces often control the resulting mechanical, tribological and functional properties. In cooperation with the Erich Schmid Institute of Materials Science (Dr. Z. Zhang, Leoben) we recently determined the atomic structure of the interface between Cu (001) and MgO (001) [25]. Cu-MgO serves as a model system for an interface which has to accommodate a large lattice mismatch – in this case more than 14%. The geometric dislocation network forms along <100> directions with Burgers vector ½ a_{Cu} <010>. Cu-O bonds which form in the coherent regions were determined to be 216 ± 8 pm in accordance with density functional calculations performed by Dr. Yao Long (Laboratory of Computational Physics, Bejing) [25]. At the Cu lattice directly adjacent to the MgO modulations of the (002) lattice plane spacing compared to bulk Cu are observed which fade of after 6 to 7 atomic layers. The resolved contraction and expansions are explained by local electronic charge redistribution causing alternating repulsive and attractive forces. In addition, the strain field of the misfit dislocations leads to large rearrangements in the atomic Cu distances adjacent to the dislocation cores with up to 60 pm difference between the shortest and longest Cu-Cu separation distance [25]. Such high precision measurements became only possible with the new generation of TEM instrumentations due to the spherical aberration correction of the imaging system.

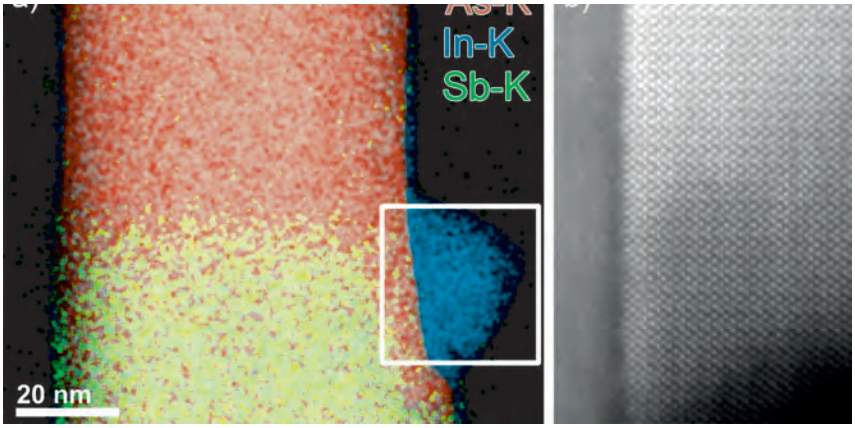


Fig. 10: *a) Interface of a semiconducting InAs-InAsSb nanowire resolved by STEM-EDS. An In-rich droplet is observed to form at the interface between the Sb-rich and Sb-lean regions. b) An atomic resolution HAADF-STEM image of a similar droplet resolving its lattice structure. The project is in cooperation with Dr. P. Krogstrup, University of Copenhagen, Denmark, providing the nanowire samples.*

Outlook. In the next years, the research of the Advanced TEM group will focus on several themes where high precision structural, chemical, and bonding information is required - embedded in close collaborations within MPIE - to advance the understanding of materials properties. This includes:

- A fundamental investigation of the atomic structure of interfacial phenomena and the impact of segregation, temperature and mechanical load on the interfacial structure.

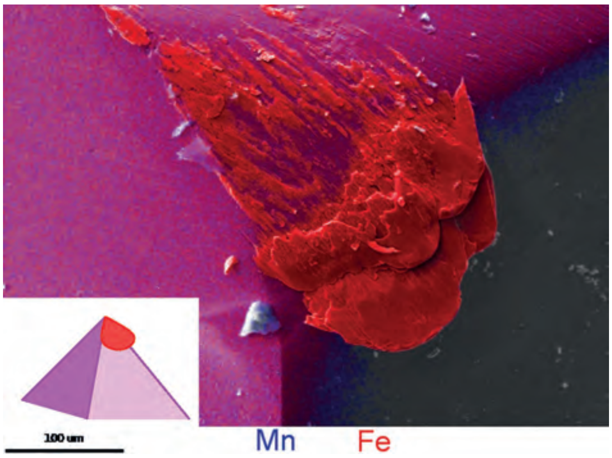


Fig. 11: *Adhesion of Fe on a stainless steel microasperity after scratching. The ferrite is coloured in red, while the stainless steel is a mixture of the blue manganese and red ferrite. The EDS map is overlayed on the SE-SEM image.*

- Coupling of atomic resolution imaging with the development of large-scale image simulations to reveal the three dimensional atomistic structure of complex material systems and to establish a direct connection to theoretical atomistic simulations.
- Resolving the atomic structure of substitutional and interstitial solutes in grain boundaries and their impact on the nano-scale mechanical properties (Fig. 9).
- Basic investigation and understanding of the deformation behaviour of nano-sized microstructures and defect/interface interactions.
- The effect of alloying behaviour on the atomic and electronic structure in metastable phases, the corresponding microstructural stability and related mechanical properties.
- The design and generation of interface dominated materials with hierarchical microstructure for structural and functional applications.
- Atomic scale chemical and defect analysis in semiconducting nanowires with a correlation to the functional properties (Fig. 10).

Nanotribology (S. Brinckmann)

Group mission. The microstructure evolution during friction and wear is at the heart of this research group. The projects research the tribological behaviour on the micrometer scale to fundamentally understand the irreversible mechanisms that result in the energy and structural loss. The investigated evolution processes include grain refinement, plasticity especially at the surface, phase formation and dissolution. In addition to the microstructural formation, a constant focus of our research is an in-depth understanding of the friction coefficient and wear rate at the micrometer scale and the controlling mechanisms. Although we mainly focus on the dry contact of metals with an infinitely hard micrometer asperity, some projects probe the metal on metal contact in the presence and absence of lubricants. The initial and evolving surface roughness is of significant importance at the micrometer-scale. The environmental control and environmental induced surface layer evolution is taken into consideration. Recently, we started to investigate the effects of hydrogen on plasticity and fracture during tribology.

Research progress. In 2014 a nanoindenter Agilent/Keysight G200 was purchased, which allows to measure tangential forces and the quantification of the friction coefficient at the micro- and nanometer length scale with the addition of the nano-vision stage (see also “New Scientific Laboratories and Facilities”, “Nanoindentation and -tribology Laboratory”). In combination with the physical setup of the laboratory, methods for surface preparation, scratch testing and post-deformation surface topography identification were optimized. One primary benefit of the nanotribology research are the high-throughput experiments: the scratch velocity, normal force and scratch repetition can be varied on a micrometer-sized area. Hence, all experiments are using the identical material and possibly identical crystal orientation. Moreover, the asperity radius and the counter material (see Fig. 11) can be varied on the same material and with the same lubricant.

We started a number of current research projects ranging from delamination testing of PtIr thin films on WC (cooperation with Dr. P.-P. Choi, MA-Department), Mo_2BC thin films on Si (cooperation with Prof. J. Schneider, RWTH Aachen, Prof. Scheu, “Nanoanalytics and Interfaces” at the MPIE) and High Entropy Alloy thin films on Si (cooperation with Dr. K.G. Pradeep and Prof. J. Schneider, RWTH Aachen) to hardness and Young‘s modulus determination of intermetallic phases in a collaboration within the SN-Department. Three primary research results are summarized below.

Elasticity and fracture during tribology. During scratching in austenite, we found that the elastic and plastic depth is given by the Hertz and hardness definition, respectively, both of which were developed for static indentation although scratching is a dynamic process [14]. We identified three domains of tribology at the micrometer scale: wear particles form for high normal forces and these wear particles lead to additional compliance; crystal orientation dependent plastic plowing dominates for medium normal forces; and the microstructure and phase distribution determine the friction at the low normal

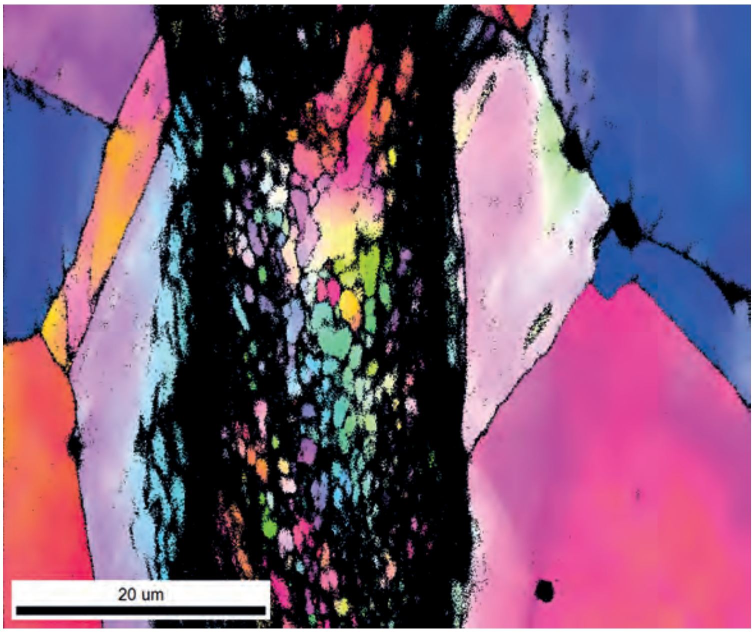


Fig. 12: *Grain refinement in coarse Cu after scratching. The scratch track is a fine-grained microstructure present after a single stroke scratch with a 20 µm indenter tip.*

forces [15]. Additionally, we observed crack formation and grain refinement (see Fig. 12) during single stroke experiments in other FCC metals.

Hydrogen embrittlement in nanotribology. We investigated the hydrogen embrittlement during tribology in Fe-Cr alloys, which were designed and produced in the MA-Department. To this end, we constructed a three-electrode electro-chemical cell for the G200. Initially, we investigated the pop-in behaviour during nanoindentation as a function of the electro-chemical charging and as a function of the grain orientation. During the scratching experiments, we observed that the surface roughness

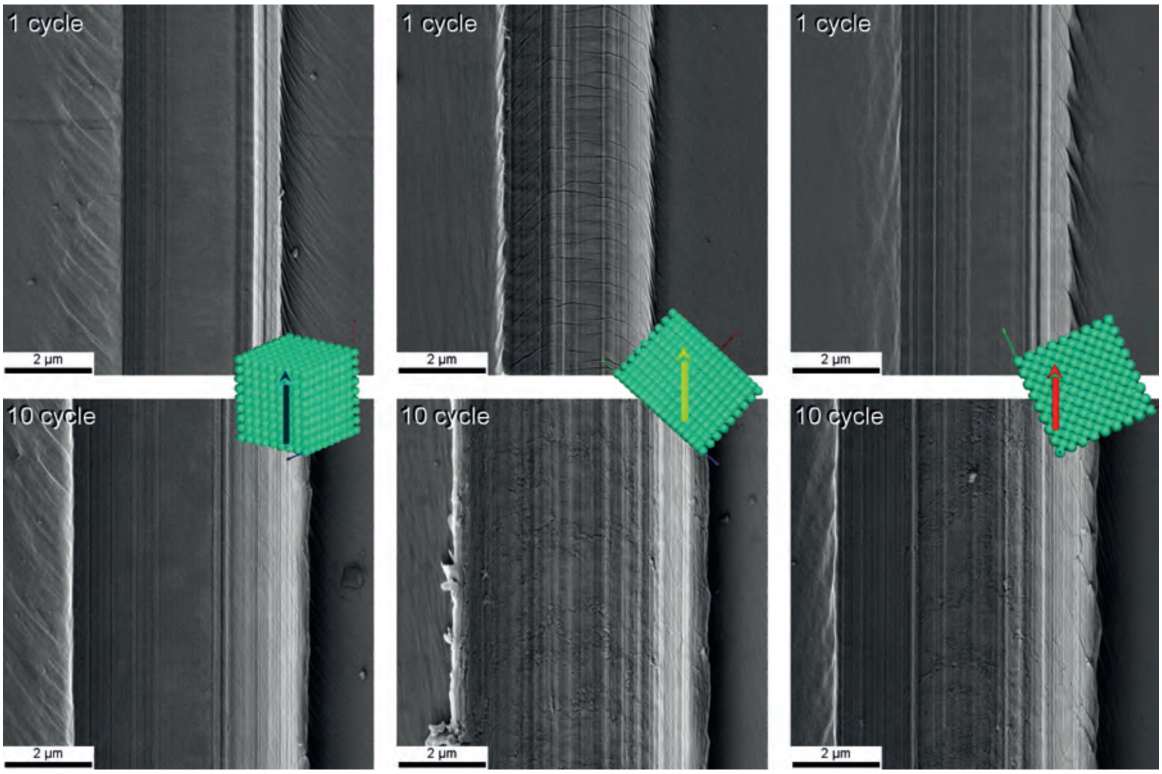


Fig. 13: *Single and repeating scratches in FeCr15 with 10 mN and 10 µm/s. The scratches are placed in different grain orientations. The center grain shows cracks already after the first scratch. After 10 cycles the scratch tracks significantly widened. In the center and right-hand image wear particles have developed.*

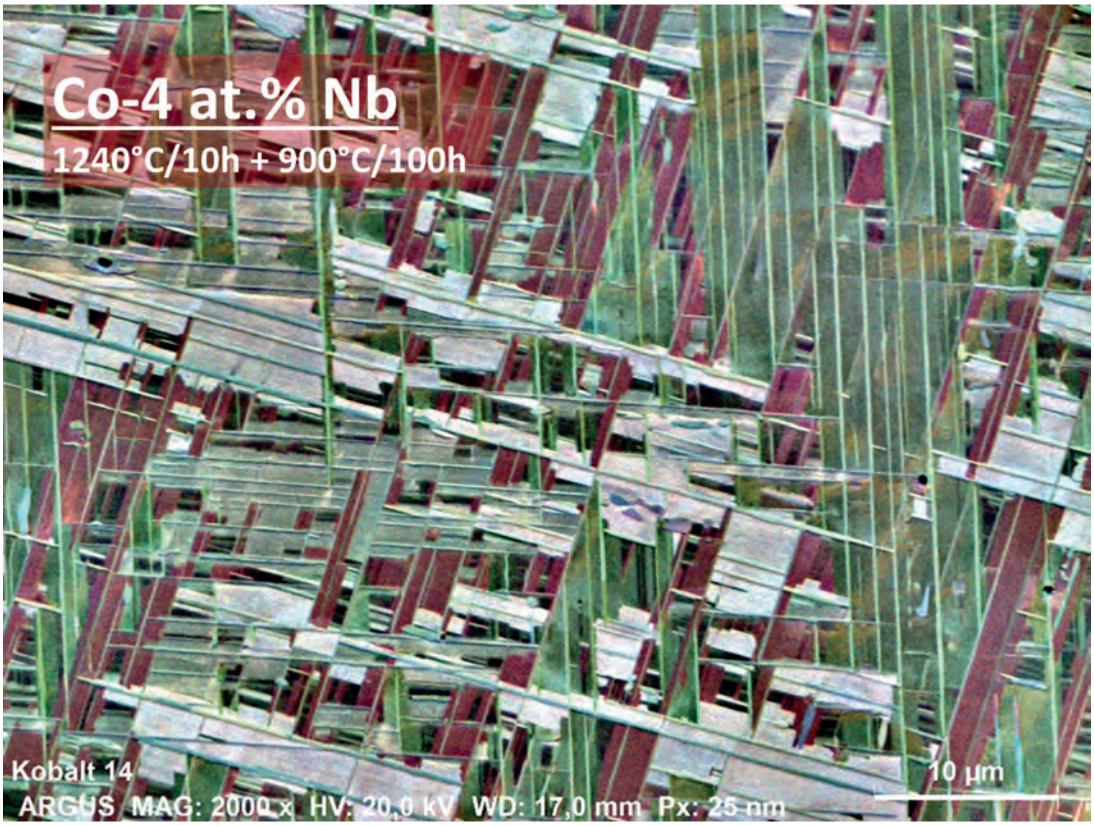


Fig. 14: *Widmanstätten-like morphology of needle-shaped intermetallic phase precipitation from super-saturated Co(Nb) solid solution. Different colours indicate different crystallographic orientations of the Co matrix. The picture was taken with a Zeiss Merlin SEM in FSD mode (image recorded by K. Angenendt).*

depends on the load order: initial scratching and subsequent polarization results in a rougher surface than initial polarization and subsequent scratching, as shown in Fig. 13.

Microstructure modifications. Most advanced bulk and thin film materials have a microstructure, which consists of fine and homogeneously distributed phases. The chemical and resulting microstructural stability is the key challenge in applying these materials in tribological applications, as friction and wear can lead to mechanical mixing and the introduction of dislocations, which would result in phase dissolution. We use pearlitic steel to study the stability of cementite and ferrite lamellae upon scratching. After scratching the surface, we investigate the microstructural stability on the surface and sub-surface in the material. In addition to investigating the tribological induced microstructure, we investigate the relation of phase boundary orientation on the friction and wear properties. With respect to pearlite, we investigate how the lamellae orientation determines the friction coefficient. The goal of this study is to fundamentally understand the friction behaviour of pearlite, which could lead to optimizing the microstructure to minimize friction and wear.

Intermetallic Materials (M. Palm, F. Stein)

Group mission. According to the Intermetallic Materials group´s mission, current research encompasses projects on fundamental aspects of phase stability and phase transformations of intermetallic phases as well as projects on establishing their properties in view of potential industrial applications. Most of the fundamental investigations are carried out in international collaborations while the more application-oriented projects are collaborations with industries.

Fundamental aspects of phase stability and phase transformations. Regarding alloy systems, the main focus of the group´s activities lies in research on iron aluminides. One of the unsolved fundamental questions in the Fe-Al system is the nature of the K-phase state (K for the German word ‘komplex’, which in this connection may be translated as ‘difficult’). The K-phase state exists between 250 and 400 °C and at Al contents between ~10 and 20 at.%, where a chemical structure occurs which shows an anomalous behaviour with respect to lattice parameters, electrical resistivity, magnetic properties and thermal dilatometry. This state was first described in 1950 and though it has been the topic of numerous investigations since then its exact nature is still unclear. With atom probe tomography

(APT) now a tool for direct observation of chemical order exists. In a collaboration with the Australian Centre for Microscopy and Microanalysis at the University of Sydney and the MA-Department at MPIE, well-defined samples were investigated by APT. Though the measurements did not reveal the existence of nano-sized, ordered regions/particles, the employed method of determining chemically sensitive, generalised multicomponent short-range order (GM-SRO) parameters by shell-based analysis of the three-dimensional atomic positions has general relevance for other alloy systems where quantitative chemical-structure evaluation of local atomic environments is required [26].

Also in the Fe-Al system, but for alloys with about 55 to 65 at.% Al, the eutectoid transformation Fe_5Al_8 (ε) ↔ FeAl + $FeAl_2$ has been studied [27-29]. This rapid solid-state reaction leads to very fine-scaled lamellar microstructures with average lamellar spacing of about 200 nm. In Ti-Al-based alloys, such microstructures lead to a combination of well-balanced properties in terms of creep, ductility and strength. However, there is limited knowledge about the properties of Fe-Al-based alloys in this composition range. Therefore, a series of as-cast as well as heat-treated alloys was analysed by SEM, electron-probe microanalysis (EPMA), XRD and differential thermal analysis (DTA). This ongoing research already led to an improved understanding of the composition dependence of all transition temperatures of the involved phases [27]. The coarsening behaviour of the lamellae at high temperatures is studied in detail and first results on the kinetics of this process are described on p. 151.

A combination of systematic experiments and calculations according to established theories for the interaction between solute atoms and dislocations has been performed to understand the strong solid solution hardening effect of V in Fe-Al. Comparison to Fe-Al-V-C alloys strengthened by V_8C_7 shows that a considerable volume fraction of carbide precipitates is needed for obtaining a comparable yield strength. However, such marked volume fractions of carbides are not desirable as they can lead to the formation of coarse, anisotropic shaped precipitates, which may act as sources for crack nucleation [30]. Also in view of the potential application of iron aluminide based alloys, the microstructure/property relationships of Fe-Al-Li and Fe-Al-Ti-B-(Mo,W) alloys have been established and the effect of Zr on the high-temperature cyclic oxidation behaviour of Fe_3Al-based alloys has been studied [31-33].

By thermal analysis (DTA and differential scanning calorimetry (DSC)), solidification behaviour and invariant reactions in a number of Fe-, Co- and Cr-based systems were studied [27,34-38]. Precise measurements of the solidus-liquidus intervals of various steel types were performed by DTA/DSC and used as a basis for the development of an improved Scheil-Gulliver model to predict the solidification temperatures of steels [34]. Isothermal sections and liquidus surfaces of the ternary systems Fe-Al-Nb [35], Cr-Al-Nb [36], and Co-Si-Ti [37] were established by combining results from thermal analyses with phase analyses from EPMA and XRD.

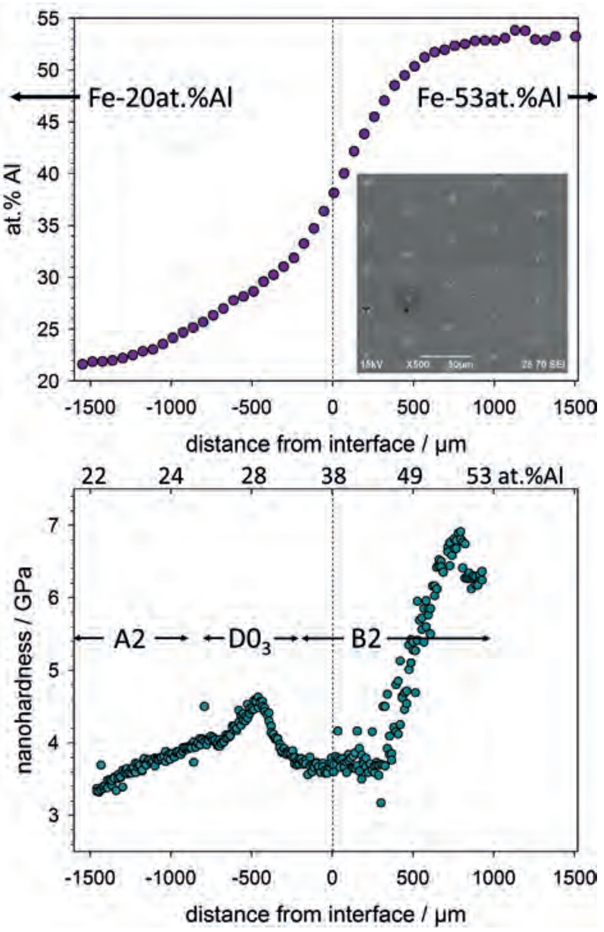


Fig. 15: *Composition dependence of the nanohardness of disordered Fe(Al) solid solution (A2) and its ordered variants $D0_3$ Fe_3Al and B2 FeAl as measured along a continuous concentration profile in a Fe-20at.%Al / Fe-53at.%Al diffusion couple. The micrograph shows an array of nanoindents in the diffusion zone.*

Based on own extensive experimental results obtained within the inter-institutional Max Planck Society research initiative ''The Nature of Laves Phases'' and critically assessed literature data the systems Co-Al, Co-Nb, Al-Nb and Co-Al-Nb were thermodynamically modeled by the Calphad method [38,39]. Two-sublattice models were used for the three Laves phase polytypes – hexagonal C14 and C36 and cubic C15 – to enable a realistic description of their homogeneity ranges in the Co-Nb and Co-Al-Nb systems. The Al-Nb and Co-Al systems were re-assessed for a better description of the homogeneity ranges of Nb_2Al and B2 CoAl, respectively. The comparison between calculated and experimental values shows that the optimized set of thermodynamic parameters gives a complete and consistent thermodynamic description of the whole Co-Al-Nb system [39].

Besides phase equilibria, also the kinetics of phase transformations and precipitation is a topic of the group. As an example, Fig. 14 shows the discontinuous precipitation of a complex intermetallic phase (whether this is monoclinic Co_7Nb_2 or hexagonal C36-type $NbCo_2$ Laves phase still has to be clarified) from a supersaturated Co solid solution. The binary Co-4at.%Nb alloy first was solution heat-treated for 10 h at 1240 °C to obtain single-phase fcc Co solid solution, and then hold at 900 °C for 100 h outside of the single-phase field to observe the discontinuous precipitation reaction.

Properties and application of intermetallics. Another focus of the group's work lies on studying the composition dependence of mechanical properties of intermetallic phases. In order to get well-defined and well-comparable, single-phase and single-crystalline material, diffusion couples are prepared from different metals or intermetallic phases and various micromechanical tests are planned to be performed along the concentration profiles obtained in the resulting diffusion zones. A first result of this ongoing project is shown in Fig. 15. By contacting pieces of Fe-Al alloys with 20 and 53 at.% Al at 1000°C for 100 h and slow cooling to room temperature, an extended continuous Al concentration profile has been obtained including the composition ranges of the disordered A2 Fe solid solution and the $D0_3$- and B2-ordered intermetallic phases Fe_3Al and FeAl. With the help of the nanotribology group, nanohardness measurements were performed along the concentration gradient. In the disordered A2 Fe(Al) composition range, the effect of solid solution hardening is clearly visible. As soon as the $D0_3$-type Fe_3Al phase occurs, a stronger increase in hardness is observed related to the effect of ordering. Within the composition range of the B2 FeAl phase, another very strong increase in hardness occurs. As the B2 FeAl phase is well known for its high vacancy concentration leading to strong vacancy hardening, the observed nanohardness increase can be expected to be related to the high density of vacancies. More detailed studies on that are ongoing.

As iron aluminides are considered as an economic replacement for stainless steels, their industrial manufacturing and evaluation of the resulting properties has become an important research topic. Within various collaborations with industries the casting of large brake discs for windmills, the rolling of different products and the forging of compressor blades has been investigated. It has also been shown that additive layer manufacturing (ALM) of iron aluminide based alloys by selective laser melting (SLM) and laser metal deposition is feasible [40]. Furthermore, in bi-lateral projects with industries, single-phase materials of the Al-rich Cu-Al intermetallic phases have been synthesised and characterised to establish fundamental physical properties, and phase equilibria in the Nb-based, high-melting Nb-Al-Fe systems are established.

References

1. Jaya, B.N.; Kirchlechner, C.; Dehm, G.: J. Mater. Sci. 30 (2015) 686.
2. Schnabel, V.; Nagamani Jaya, B.; Köhler, M.; Music, D.; Kirchlechner, C.; Dehm, G.; Raabe, D.; Schneider, J.M.: “Damage-tolerant glasses defined by deep core electronic hybridization“, *submitted* (2015).
3. Wimmer, A.; Smolka, M.; Heinz, W.; Detzel, T.; Robl, W.; Motz, C.; Eyert, V.; Wimmer, E.; Jahnel, F.; Treichler, R.; Dehm, G.: Mater. Sci. Eng. A 618 (2014) 398.
4. Imrich, P.; Kirchlechner, C.; Motz, C.; Dehm, G.: Acta Mater. 73 (2014) 240.
5. Imrich, P.; Kirchlechner, C.; Dehm, G.: Mater. Sci. Eng. A 642 (2015) 65.
6. Imrich, P.; Kirchlechner, C.; Motz, C.; Dehm, G.: JOM 67/8 (2015) 1704.
7. Imrich, P.; Kirchlechner, C.; Motz, C.; Dehm, G.: Scr. Mater. 100 (2015) 94.
8. Brinckmann, S.; Völker, B.; Dehm, G.: Int. J. Fract. 190 (2014) 167.
9. Jeon, J.B.; Dehm, G.: Scr. Mater. 102 (2015) 71.
10. Völker, B.; Heinz, W.; Matoy, K.; Roth, R.; Batke, J.M.; Schöberl, T.; Cordill, M.J.; Dehm, G.: Thin Solid Films 583 (2015) 170.
11. Völker, B.; Venkatesan, S.; Heinz, W.; Matoy, K.; Roth, R.; Batke, J.M.; Cordill, M.J.; Dehm, G.: J. Mater. Res. 30 (2015) 1090.
12. Völker, B.; Heinz, W.; Roth, R.; Batke, J.M.; Cordill, M.J.; Dehm, G.: Surf. Coat. Technol 270 (2015) 1.
13. Völker, B.; Heinz, W.; Matoy, K.; Roth, R.; Batke, J.M.; Schöberl, T.; Scheu, C.; Dehm, G.: Philos. Mag. 95 (2015) 1967.
14. Brinckmann, S.; Fink, C.A.C.; Dehm, G.: Wear 338-339 (2015) 430.
15. Brinckmann, S.; Dehm, G.: Wear 338-339 (2015) 436.
16. Marx, V.M.; Kirchlechner, C.; Zizak, I.; Cordill, M.J.; Dehm, G.: Philos. Mag. 95 (2015) 1982.
17. Marx, V.M.; Toth, F.; Wiesinger, A.; Berger, J.; Kirchlechner, C.; Cordill, M.J.; Fischer, F.D.; Rammerstorfer, F.G.; Dehm, G.: Acta Mater. 89 (2015) 278.
18. Philippi, B.; Kirchlechner, C.; Micha, J.S.; Dehm, G.: ”Size and orientation dependent mechanical behavior of tetragonal body-centered tin at high homologous temperatures”, *submitted* (2015).
19. Kirchlechner, C.; Imrich, P.J.; Liegl, W.; Pörnbacher, J.; Micha, J.S.; Ulrich, O.; Motz, C.: Acta Mater. 94 (2015) 69.
20. Wimmer, A.; Heinz, W.; Detzel, T.; Robl, W.; Nellessen, M.; Kirchlechner, C.; Dehm, G.: Acta Mater. 83 (2015) 460.

21. Raghavan, R.; Harzer, T.P.; Chawla, V.; Djaziri, S.; Phillipi, B.; Wehrs, J.; Wheeler, J.M.; Michler, J.; Dehm, G.: Acta Mater. 93 (2015) 175.
22. Djaziri, S.; Li, Y.J.; Nematollah, A.; Grabowski, B.; Goto, S.; Kirchlechner, C.; Neugebauer, J.; Raabe, D.; Dehm, G.: "Deformation-induced martensite in severely cold-drawn pearlitic steel: A new mechanism at play", *submitted* (2015).
23. Harzer, T.P.; Djaziri, S.; Raghavan, R.; Dehm, G.: Acta Mater. 83 (2015) 318.
24. Harzer, T.P.; Duarte, M.J.; Raghavan, R.; Dehm, G.: "*In-situ* TEM study of diffusion kinetics and electron irradiation effects on the decomposition of a nanocrystalline Cu– 4 at.%Cr thin film", *in preparation* (2015)
25. Zhang, Z.; Long, Y.; Cazottes, S.; Daniel, R.; Mitterer, C.; Dehm, G.: Sci. Rep. 5 (2015) 11460.
26. Marceau, R.K.W.; Ceguerra, A.V.; Breen, A.J.; Palm, M.; Stein, F.; Ringer, S.P.; Raabe, D.: Intermetallics 64 (2015) 23.
27. Li, X.; Palm, M.; Scherf, A.; Janda, D.; Heilmaier, M.; Stein, F.: MRS Online Proc. Lib. 1760 (2015) mrsf14-1760-yy04-09.
28. Scherf, A.; Janda, D.; Baghaie Yazdi, M.; Li, X.; Stein, F.; Heilmaier, M.: Oxid. Met. 83 (2015) 559.
29. Reiche, H.N.; Carpenter, J.S.; Stein, F.; Tomida, T.; Vogel, S.C.: Can. Metall. Q. 54 (2015) 2.
30. Kratochvíl, P.; Pešička, J.; Král, R.; Švec, M.; Palm, M.: Metall. Mater. Trans. A46 (2015) 5091.
31. Li, X.; Stein, F.; Palm, M.: MRS Symp. Proc. 1516 (2013) 263.
32. Li, X.; Prokopčáková, P.; Palm, M.: Mater. Sci. Eng. A611 (2014) 234.
33. Hotař, A.; Kejzlar, P.; Palm, M.; Mlnařík, J.: Corros. Sci. 100 (2015) 147.
34. Schaffnit, P.; Stallybrass, C.; Konrad, J.; Stein, F.; Weinberg, M.: CALPHAD 48 (2015) 184.
35. Stein, F.; He, C.; Prymak, O.; Voß, S.; Wossack, I.: Intermetallics 59 (2015) 43.
36. Stein, F.; He, C.; Wossack, I.: J. Alloys Compd. 598 (2014) 253.
37. Krendelsberger, N.; Weitzer, F.; Schuster, J.C.; Stein, F.: Intermetallics 38 (2013) 92.
38. Stein, F.; He, C.; Dupin, N.: Intermetallics 39 (2013) 58.
39. He, C.; Stein, F.; Palm, M.: J. Alloys Compd. 637 (2015) 361.
40. Rolink, G; Vogt, S.; Senčekova, L.; Weisheit, A.; Poprawe, R.; Palm, M.: J. Mater. Res. 29 (2014) 2036.

Research Projects in Progress

Nano-/Micromechanics of Materials (C. Kirchlechner)

Balila, Kirchlechner, Dehm: Reliability of fracture toughness test geometries at the micron-scale

Balila, Kirchlechner, Dehm: Deformation and fracture of interfaces in metallic materials

Balila, Kirchlechner, Dehm (in cooperation with M. Köhler, D. Raabe, MA-Department; J. Schneider, D. Music, V. Schnabel, RWTH Aachen): Fracture behavior of metallic glass thin films

Balila, Kirchlechner, Dehm (in cooperation with J. Michler, EMPA Thun, Switzerland): High temperature fracture mechanics

Davydok, Kirchlechner: Dislocation-grain boundary interaction studied by X-ray µLaue diffraction: The role of stacking fault energy

Djaziri, Kirchlechner, Dehm (in cooperation with J. Schneider, RWTH Aachen): Measuring fracture strain of Mo_2BC

Djaziri, Kirchlechner, Dehm (in cooperation with Y.J. Li, D. Raabe, MA-Department; S. Goto, Akita University, Japan): Shedding light on nanostructured pearlitic steel by advanced X-ray characterization

Kirchlechner: Micron-sized cantilevers and the Bauschinger effect

Kirchlechner (in cooperation with G. Pharr, UT Knoxville, TN, US): Probing dislocation grain-boundary interaction(s) by indentation pop-in statistics

Malyar, Dehm, Kirchlechner (in cooperation with J.-S. Micha, CEA-Grenoble): Dislocation slip transfer in micron-sized bi-crystals analyzed by advanced *in situ* methods

Marx, Kirchlechner, Dehm (in cooperation with M. Cordill, Erich Schmid Institut für Materialwissenschaft, Leoben, Austria): Temperature effects on the mechanical behavior of single and multilayer thin films on flexible substrates

Philippi, Kirchlechner, Dehm: Thermo-mechanical investigation of solder joints

Raghavan, Dehm (in cooperation with C. Tasan, MA-Department): Electroplasticity in metals

Raghavan, Harzer, Dehm: Plasticity of co-evaporated and sputtered multi-layered copper-chromium film

Raghavan, Kirchlechner, Dehm (in cooperation with M. Feuerbacher, FZ Jülich): Plasticity in fcc high entropy alloys

Soler, Harzer, Kirchlechner, Dehm (in cooperation with P. Mayrhofer, M. Bartosik, TU Wien, Austria): Role of bi-layer period on the mechanical response of a CrN / TiN multilayer

Soler, Harzer, Venkatesan, Kirchlechner, Liebscher, Dehm: Mechanical response of colloidal gold particles studied *in situ* in the TEM

Soler, Venkatesan, Dehm (in cooperation with several companies within the ENIAC Joint Undertaking EPPL): Global and local fracture properties of interfaces at variable temperature for robust material combinations in power devices

Subramanian, Kirchlechner: Algorithms for investigating satellite peaks in Laue patterns

Taniguchi, Kirchlechner, Liebscher, Dehm: Dislocation-precipitate interaction mechanisms

Advanced Transmission Electron Microscopy (C. Liebscher)

Harzer, Liebscher, Scheu, Dehm (in cooperation with T. Dennenwaldt, Interdisciplinary Center for Electron Microscopy, Ecole polytechnique fédérale de Lausanne): Electron energy loss spectroscopy of bcc-Cu in Cu-Cr thin film structures

Harzer, Djaziri, Raghavan, Dehm: Nanostructure, chemical composition, and mechanical properties of Cu-Cr thin film structures

Liebscher, Dehm: TEM investigation of sulfur segregation in Cu grain boundaries

Peter, Kirchlechner, Liebscher, Dehm: Dislocation grain boundary interaction in Cu grain boundaries studied by *in-situ* TEM

Soler, Venkatesan, Kirchlechner, Liebscher, Dehm: *In-situ* TEM deformation studies on nanoparticle systems

Stoffers, Cojocaru-Mirédin, Liebscher, Raabe, Scheu, Dehm: Atomic structure of segregation effects at grain boundaries in multicrystalline silicon

Venkatesan, Soler, Dehm: Global and local fracture properties of interfaces and their correlation to microstructure in electronic power devices

Venkatesan, Liebscher, Scheu, Dehm (in cooperation with P. Krogstrup, Center for Quantum Devices, Niels Bohr Institute, University of Copenhagen, Denmark): Atomic scale chemical and defect structure investigation of MBE grown III-V semiconducting nanowires

Nanotribology (S. Brinckmann)

Brinckmann, Dehm: Nanotribology in austenite and copper

Duarte Correa, Brinckmann, Dehm: Crystallization kinetics and microstructural evolution of metallic glasses

Duarte Correa, Brinckmann, Dehm: Corrosion and wear at the nanoscale

Fink, Brinckmann, Dehm: Nanotribology of iron-alloy microstructures

McKeown, Brinckmann, Dehm: Nanoscratch-testing of thin films

Intermetallic Materials (M. Palm, F. Stein)

Azmi, Michalcová, Palm: Microstructure and mechanical properties of Fe–Al–Nb–B alloys

Li, Stein (in cooperation with A. Scherf, M. Heilmaier, KIT Karlsruhe): Al-rich Fe–Al *in-situ*-composite materials: microstructure and mechanical properties

Li, Stein (in cooperation with R. Spatschek, CM-Department): Coarsening kinetics of fine-scaled lamellar B2-FeAl + $FeAl_2$ eutectoid microstructures

Lotfian, Prokopčáková, Švec, Palm (in cooperation with Leistritz Turbinenkomponenten Remscheid GmbH; IST RWTH Aachen; Access e.V.): Forged iron aluminide turbine blades: Process development and characterisation

Luo, Kirchlechner, Dehm, Stein: *In-situ* micromechanical studies of intermetallic phases along concentration profiles in diffusion couple zones

Marx, Palm (in cooperation with Winterthur Gas & Diesel Ltd.; Wärtsila Finland Oy; Wärtsila Netherlands BV; Kennametal Stellite GmbH; ABB Turbo Systems AG): Intermetallics for engine applications

Michalcová, Senčeková, Szczepaniak, Palm (in cooperation with Airbus Group Innovations; Siemens AG Corporate Technology; Fraunhofer-Institut für Lasertechnik; Dr. Kochanek Entwicklungsgesellschaft; NANOVAL GmbH & Co. KG): RADIKAL – Alloy development for and characterisation of iron aluminide components manufactured by additive layer manufacturing

Palm (in cooperation with P. Kratochvíl, J. Pešička, R. Král, Dept. Physics of Materials, Charles University Prague; M. Švec, Technical University Liberec): Basic principles of solid solution hardening in iron aluminide alloys

Palm, Stein (in cooperation with R. Wartbichler, S. Mayer, H. Clemens, Montanuniversität Leoben, Austria): The effect of Mo additions and processing on the microstructure of Al-rich Ti–Al alloys

Poková, Liebscher, Stein: TEM studies on dislocations and deformation mechanisms of Laves phases

Stein (in cooperation with A. Kaiser, Fraunhofer IKTS, Dresden): High-temperature phase equilibria and melting behavior of Nb-rich Fe–Al–Nb alloys

Stein (in cooperation with T. Horiuchi, Hokkaido University of Science, Japan): Kinetics of peritectoid decomposition reactions

Stein (in cooperation with T. Horiuchi, Hokkaido University of Science, Japan): Discontinuous precipitation of intermetallic phases from Co solid solution

Stein, Li, Liebscher (in cooperation with A. Szczepaniak, H. Springer, MA-Department; H. Becker, T. Zienert, A. Leineweber, TU Bergakademie Freiberg): Substructure formation and crystallographic transformation of the complex intermetallic phase Fe_2Al_5

Varona Caballero, Palm (in cooperation with S. Milenkovic, IMDEA Materials): Development of new generation NiAl-based eutectic composites with tuneable properties