PART II.

THE DEPARTMENTS

(in alphabetical order)

Department of Computational Materials Design

J. Neugebauer

Scientific Objective and Department Structure

The department of Computational Materials Design **develops, implements, and applies *ab initio* guided computational methodologies and toolsets that allow for an accurate prediction of properties of advanced structural and functional materials in realistic environments**. A challenge in overcoming materials limitations and designing such materials is that their technological relevant properties are typically directly related to a high complexity in chemistry, atomic geometry and microstructure. Over the last reporting period, the department has pushed the development of methods both with respect to accuracy and computational efficiency. These developments enabled *ab initio* guided atomistic approaches to handle a completely new level of complexity.

Examples are computational tools that allow us to predict materials properties up to the melting temperature for technologically highly attractive materials such as, e.g., ultra-high strength steels, light-weight alloys, high-entropy alloys, or magnetocaloric materials. This required the development of algorithms that allow us to compute the various entropic contributions - chemical, electronic, vibrational and magnetic. Several breakthroughs, often achieved through a joint effort of the scientific research groups of the

department, allow us now to include non-adiabatic coupling contributions such as electron-phonon or magnon-phonon interactions. In contrast to common belief, these mechanisms turned out to be highly relevant and crucial to describe phenomena that were hitherto out of reach for fully parameter-free *ab initio* approaches.

The **group of Tilmann Hickel** used and extended these approaches to address a wide range of technologically relevant materials topics related to high-strength steels, light-weight and Heusler alloys, magnetocaloric materials, super-conductors, as well as to systematically identify processes and failure mechanisms such as hydrogen embrittlement. Based on this broad expertise he very successfully established a large number of joint co-operations and large-scale projects with partners from industry and academia. The **group of Blazej Grabowski** successfully extended the TILD (Thermodynamic Integration using Langevin Dynamics) family of efficient thermodynamic sampling approaches to describe not only solids but also melts. In the last three years, he furthermore developed a variety of coarsegraining techniques that allowed his group to describe systems, such as grain boundaries or
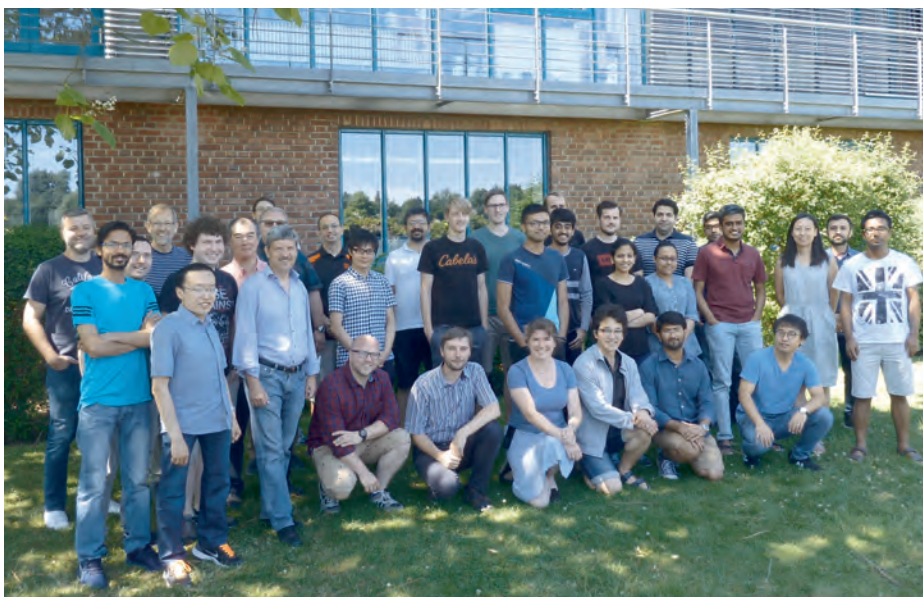

Fig. 1: *The CM department (2018).*

nano-composites consisting of millions of atoms, over large time scales. **Fritz Körmann** broadened his expertise in describing magnetic phenomena to the modelling of compositionally complex alloys in his newly (Summer 2017) founded group.

Methodological breakthroughs also opened new research opportunities in other fields: Transferring concepts from semiconductor physics to electrochemistry, the **group headed by Mira Todorova** developed an approach that allows a fully *ab initio* computation of reactions in an electrochemical cell. Using these new developments made it possible to address very fundamental questions, such as the impact of a solvent on the structure of oxide passivation layers or the fundamental mechanisms that control Mg corrosion.

Several methodological breakthroughs were also achieved in the **group of Christoph Freysoldt**. Important examples are new approaches to treat large electric fields and charges in systems with reduced dimensions or a highly efficient approach to perform atomic relaxations. The electrostatic tools provided, for example, new insight into the mechanisms controlling the resolution of atom probe tomography and an additional close link to the activities in the experimental departments. The **group of Liverios Lymperakis** achieved important methodological developments on thermodynamic and kinetic surface phase diagrams.

The **availability of our in-house developed computational methodologies and tools** provided a firm basis for highly successful collaborations with the other departments at the MPIE. These cover materials science topics such as understanding and designing, e.g., ultra-high strength steels or ductilization of Mg alloys, as well as providing new theoretical concepts such as machine learning techniques to enhance resolution and interpretation of experimental techniques (see p.53). These interdepartmental activities resulted in more than 50 joint publications over the last 6 years. They also strengthened existing and opened new collaborations with external partners, resulting in several projects funded, e.g., by the German Research Foundation (DFG), the Ministry for Science and Education (BMBF) or the EU.

This ability to address critical materials science questions by developing new methodological concepts and the respective computational tools enabled the department to publish in high-ranking journals in the Nature family, in Phys. Rev. Lett, etc. Since these highly accurate and computationally efficient approaches require highly complex simulation protocols, it was difficult to disseminate them within the department as well as to external partners. To address this issue the department developed over the last years *pyiron* [1,2] – a platform that provides an integrated development environment to implement and test these methodological tools. Pyiron provides

the users with a single standardised interface to run these complex protocols and allows easy upscaling to high throughput studies. As a result, the time needed to become acquainted with the new tools is dramatically reduced, productivity is boosted and the exchange with external partners is simplified. The new pyiron platform also turned out to be instrumental in linking the various method developments by members of the department, opening the large amount of computed data to big data analytics and machine learning.

Pyiron is provided as open source to the scientific community. Other developments are provided as open source as well. Examples are a toolbox for automatically creating arbitrary coincidence site lattice (CSL) grain boundaries [3,4] developed by Sherry Hadian or the tools [5] created by Christoph Freysoldt to compute charged defects in low dimensional systems.

The high international visibility of these developments and studies **opened prestigious job opportunities for several members of the department**. For example, Martin Friák – a former group leader – became head of a joint experimental and theoretical group at the Czech Academy of Sciences in Brno. Robert Spatschek, head of a W2 group, became professor at the RWTH Aachen and head of a section at the Forschungszentrum Jülich. Blazej Grabowski, who is currently a group leader, received an offer for a W3-professorship position at the University of Stuttgart. Former PhD students or PostDocs – Sangheon Lee, Won-Seok Ko, Poulumi Dey and Anoop Kishore Vatti – obtained assistant professor positions in Korea, the Netherlands or India. Chris Race – a former Humboldt fellow – is now a Royal Society University Research Fellow and Senior Research Fellow at the University of Manchester.

To foster collaborations with leading experts worldwide, members of the department actively engaged in initiating and organizing international workshops and symposia. Examples are the workshop on grain boundary migration (S. Hadian), the continuation of the successful biennial workshop series Ab initio Description of Iron and Steel (ADIS; T. Hickel) and the international workshop series on electrochemistry (M. Todorova, C. Freysoldt). Furthermore, several symposia at international conferences such as the DPG (T. Hickel, J. Neugebauer), MRS (J. Neugebauer), TMS (T. Hickel), MMM (J. Neugebauer, T. Hickel) or MSE (S. Hadian) were organised (see p. 232).

The broad expertise in various aspects of materials modelling made the department also very attractive for international guests: During the reporting period the department hosted two Humboldt Fellows (R. Hadian, G. Leyson) and one Humboldt Research Award winner (M. Finnis). M. Ashton just received a Humboldt Fellowship. The high quality and visibility

Fig. 2: *The ADIS2018 workshop in Ringberg was one of several workshops organized by the CM department.*

of their research enabled members of the department to **receive highly competitive and prestigious research grants**. Blazej Grabowski received an ERC starting grant. Fritz Körmann successfully applied for a VIDI-Prize of the Dutch Science Foundation.

Due to the expertise of the department in developing tools for big data analytics and advanced data storage with focus on computational materials science, members of the department became highly active in national and international community activities related to digitalization in materials science. Jörg

Neugebauer became, e.g., founder and chair of the expert committee "Digital transformation in materials engineering" of the Association of German Engineers (VDI). He was also elected as member of the DFG review board (Fachkollegiat) Materials science and chair of the German Physical Society (DPG) division "Metals and Materials".

In the following, a brief overview of the activities and research highlights of the groups in the department is given.

Research Groups

Computational Phase Studies (T. Hickel)

The group "Computational Phase Studies" 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 bulk and defect phase diagrams, which are directly related to many technologically relevant properties and processes in metals. In this context, the group again made over the last three years substantial progress in developing methods and employing them for advanced material systems. This applies in particular to the following fields of research:

- The inclusion of new thermodynamic concepts to resolve, for example, the coupling of excitation processes, the lifetime of quasiparticles, or hitherto unclear features in experimental data.

- The prediction of phase stabilities near extended defects, such as grain boundaries, stacking faults and interfaces.

- The distribution of interstitials and solutes next to extended defects, including ordering, co-segregation and de-cohesion effects.

- The chemo-mechanical coupling during precipitate growth in structural materials, such as steels and Al alloys.

- The application of the developed thermodynamic methods to novel functional material systems (Fig. 3).

The research in the group is characterized more and more by **strong collaborations** with other groups, within the CM department, with other departments of the MPIE, as well as with academic and industrial partners in various research institutions. Out of more than 40 publications published by the group within the last three years, 95% resulted from such kind of collaborations, every second having a first author from a member of the group. Large scale net-working projects like those listed in pages 65 and 67 , but also a number of consortia consisting of 3-5 members were triggered by the multiple research interests of the group. The group was further active in co-organizing international meetings, like the above-mentioned series of ADIS workshops, as well as several symposia at conferences. This also helped the group to disseminate recent scientific achievements like the once discussed in the following:
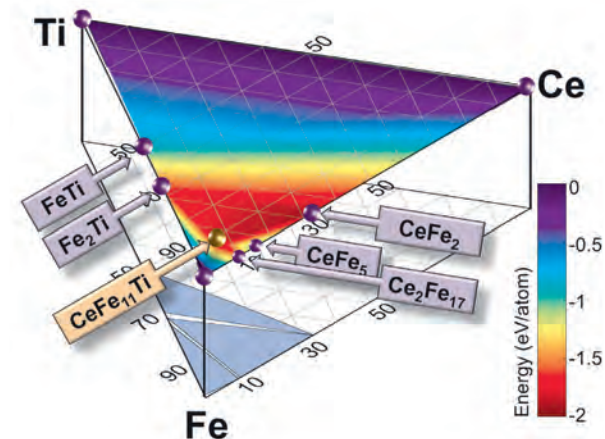
Fig. 3: *Ab initio calculated phase formation diagram for Ce-Fe-Ti alloys at 1500 K. Blue (red) color shows the energetically high (low) phases among the considered alloys.*

In the field of *ab initio* **thermodynamics** we were able to obtain several new insights. It was for example exciting to see that electron-phonon coupling is not only occurring at temperatures close to melting [6], but its explicit consideration is also required to understand experimental heat capacity data at temperatures below a few Kelvin [7] (A. Gupta). Similarly, the generalization of our methods for treating chemical disorder [8] (B. Dutta) and determining anharmonic lattice vibrations (A. Glensk) to phonon linewidths required intensive interactions with experimental colleagues. Only after unifying the physical concepts behind data evaluation, highly precise *ab initio* molecular dynamics has resulted into an amazing agreement with inelastic neutron scattering.

Recent efforts were spent on the interaction of magnetic excitations with lattice degrees of freedom. Close to the critical magnetic temperature, this interaction turned out to have a substantial impact on phonon linewidths [9]. Even the static relaxation of atomic positions next to a vacancy in paramagnetic iron was found to be highly non-trivial (see p. 197). Only the combination of the flexible IDE pyiron [2] (see above) to handle large sets of magnetic configurations, the recent implementation of constrained magnetic moments into our in-house DFT code SPHInX (see below) and the spin-space averaging approach developed in our group allowed us to handle this challenge (O. Hegde, O. Waseda). The success of this approach triggered its application to more complex materials such as Fe-based superconductors (F. Lochner).

The main purpose of these efforts remains to be the computation of phase stabilities and phase diagrams [10,11]. One of the promising strategies is to use our *ab initio* determined heat capacity as an input for Calphad assessments [12] (A. Zendegani). More interesting is, however, the consideration of Gibbs energies that are directly obtained by DFT. Our phase diagrams for magnetocaloric Heusler al-

loys computed in this way demonstrate that we can not only predict the chemical dependence of the martensitic transition temperature [13], but can also understand the origin of intramartensitic transitions between different twinned substructures (B. Dutta) [8,14]. To automatize such complex evaluations in the future, we develop algorithms that take the precision in the Gibbs energy as a convergence goal and automatically determine the convergence parameter to achieve it (J. Janßen).

The formation of **planar defects** such as twin boundaries and stacking faults [6,15] will give rise to structures, which are not part of bulk phase diagrams. We have identified such reconstructions, for example for twin boundaries in Mg [16], by mapping the gamma surface of all possible displacements of the neighbouring grains (Z. Pei, Fig. 4). Particularly fascinating, however, is the structure of defects in Fe_2Nb Laves phases (see p. 173). Here, the formation of stacking faults is enhanced by the enrichment of Nb in the material. This phenomenon, analysed with high-resolution TEM in the SN department, could be explained thermodynamically (A. Zendegani), by generalizing bulk concepts of phase decomposition to defect structures.
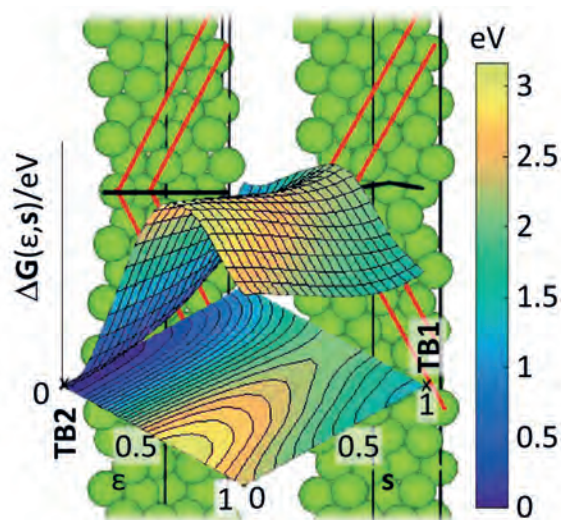
Fig. 4: *Gibbs energy gamma surface for {1011} compression twins in pure Mg [16].*

In this material, as in many other systems investigated within the group, the magnetic interactions add another level of complexity to the system. We often observe that structural stabilities depend on the magnetic state [17]. A careful analysis of this coupling in bulk materials gives occasionally the decisive clue for understanding also the reconstruction at the defects. In this way, we resolved for example a longstanding mystery about the thickness dependence of magnetism in Fe films grown on Cu(001) (X. Zhang) [18]. Nevertheless, the treatment of magnetism next to defects often requires its own methodological concepts, some of which we have developed for example

THE DEPARTMENTS

for the case of stacking faults in high-Mn steels (I. Bleskov) [19]. They are currently being generalized by machine learning techniques (O. Waseda). Altogether, the interplay of structure, chemistry and magnetism makes the thermo-dynamics of planar defects currently a comprehensive research topic of the group.

The **segregation of interstitials** next to planar defects is strongly linked to this topic. Interesting for steels is, for example, how C is redistributed if the phase boundary between austenite and martensite starts moving upon cooling. We realized that the path along which the structure transforms is decisive for the degree of Zener ordering in the virgin martensite (X. Zhang) [20].

Conversely, solutes such as H can have a decisive impact on the stability of planar defects in steels (see p. 177). We have extended our long-standing experience in investigating this detrimental effect (E. McEniry, S. Sreekala, A. Tehranchi) [21] by four major developments: (i) We have looked into co-segregation effects [22], including in particular the important competition between H and C [23]. (ii) We have performed tensile tests in order to study the decohesion and crack formation at a matrix-precipitate interface with and without H [24]. (iii) We have considered the impact of imperfections such as misfit dislocations in matrix-precipitate interfaces [25]. Finally, (iv) we have developed various coarse-grained and multiscale approaches to go beyond the scale accessible by *ab initio* calculations [26]. This spectrum of insights was beneficial for several industrial collaborations and further boosted our recognition in the community, e.g., by involving us in all major conferences in this field.

The **chemo-mechanical coupling** processes at the interface between precipitate and matrix have been further investigated (P. Dey) for kappa carbides $(Fe,Mn)_3AlC$, which form elaborate superstructures in high-Mn steels. We have explained the reduced C content observed experimentally with atom probe tomography in the MA department, to be mainly a result of the coherency strain in the carbide [27]. As we have shown, the C depletion has consequences for several other interesting phenomena, such as the change of anisotropy in the Young modulus and the resulting particle orientation in the superstructure [27], the formation of Mn antisites [28] as well as the reduction of the antiphase boundary energy and the resulting higher propensity for shearing by dislocations [29]. Interestingly, even the distribution of the C atoms that are consequently solved in the Fe matrix material is strongly influenced by the coherency strain, as resolved by a correlative APT-TEM-DFT study [30] (see p. 181).

To circumvent some of the challenges of steels, we used the prototype system of Al_3Sc particles in Al alloys to study chemo-mechanical coupling dur-

ing particle growth (A. Gupta). In combination with radio tracer diffusion experiments, we were able to proof that a solute atom approaching the growing precipitate will be influenced by the coherency strain and segregation effects of the latter (Fig. 5), reducing the effective diffusion rate of the solute [31]. This needs to be taken into account when performing kinetic simulations of TTT diagrams. Further, our multiscale simulations have shown that size-dependent concentration gradients in the matrix phase next to the precipitate can yield surprising phenomena like inverse ripening, where the smaller precipitates grow at the expense of the larger ones [32].
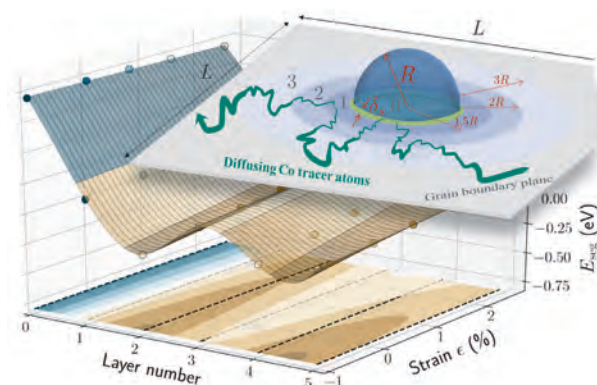
Fig. 5: *Schematic illustration of the employed diffusion model for Sc tracer particles (inset) together with the particle segregation energy surface in the misfit strain field of a Al_3Sc nanoprecipitate [31].*

Many of the techniques and concepts discussed above have originally been developed for unary metals [33] or steels [34], but have been meanwhile transferred to a variety of further **functional materials** with high relevance for applications. For example, the incorporation of the interstitial element H into a crystal structure and the impact on its vibrational spectrum has been analysed for pentlandite $(Fe_{4.5}Ni_{4.5}S_8)$ [35], which is a promising electro-catalyst for hydrogen evolution reactions (A. Zendegani). The interaction of structure and magnetism is important for magnetic shape-memory and magnetocaloric material systems [36]. Here, in particular magnetocrystalline anisotropies [37], concepts of disorder [38] and the impact of interfaces where martensitic transformations take place have been recently studied (B. Dutta, N. Shayanfar). One of the most recent developments is our (F. Lochner) application of these techniques to unconventional superconductors [39]. In particular, the methods developed for structural relaxations in a paramagnetic state have the potential to improve the performance of DFT for Fe-based superconductors substantially and to explain the nematic phase transitions observed there.

The various concepts of *ab initio* thermodynamics and in particular of treating magnetic excitations have been successfully applied to Ce-based hard magnetic materials (H. Sözen, Fig. 3). We were able

to show at which temperatures the promising hard-magnetic phase $CeFe_{11}Ti$ decomposes into pure Fe and the Laves phases $CeFe_2$ and Fe_2Ti, and how this detrimental effect can be influenced by changing the chemical composition. This example opens a new route of *ab initio* based materials design, which is currently extended to high-throughput and machine learning techniques.

Adaptive Structural Materials (B. Grabowski)

The general aim of the Adaptive Structural Materials (ASM) group is the design of advanced, next-generation structural materials based on innovative concepts driven by state-of-the-art simulation tools. To this end, the ASM group employs and further advances the methods developed in the CM department over the past years. The methods are rooted in accurate *ab initio* approaches and extend to large-scale molecular dynamics simulations based on empirical potentials and to analytical approaches based on continuum theory. The group has a strong collaborative network within the MPIE (e.g., Nano-/Micromechanics of Materials group in the SN department) and with external partners from academia (e.g., Imperial College London, KTH Stockholm, Linköping University, or Skoltech Moscow) and industry (Sandvik, Sweden). The projects investigated in the ASM group extend 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. The group activities are supported by the ERC Starting Grant TIME-BRIDGE (see p. 71).

A core effort of the ASM group is the development of efficient *ab initio* methods for a **highly accurate free energy determination at finite temperatures**. This work is carried out in close collaboration with the Complex Concentrated Alloys (CCA) and Computational Phase Studies (CPS) group. One example is the calculation of highly accurate stacking fault energies up to the melting temperature (X. Zhang) as required, e.g., for the design of Ni based superal-loys for airplane turbines [6]. Another example is the thermodynamic description of dynamically unstable systems (Fig. 6; D. Korbmacher). In particular, we were recently able to develop a method that allows us to compute efficiently and accurately spectrally resolved quantities such as phonon frequencies (Fig. 9). Furthermore, a new method was developed for the accurate treatment of the coupling between vibrations and magnetic excitations [9] (I. Stockem, in collaboration with B. Alling from Linköping University). Further efforts have been directed to extend the methods to liquids (L. Zhu), which has enabled an accurate determination of melting properties from *ab initio* (TOR-TILD method; [49]). Recently, efforts have been undertaken to extend our methods also to kinetic properties, specifically temperature-dependent free energy barriers (L. Huber and R. Dsouza).

Many group activities have been focused on **large-scale simulations**. Within our SPP project on self-healing metals (SPP 1568), we have for example investigated the transformation behaviour of Ti-Ni shape-memory nanoparticles embedded in a Ni-Ti-V matrix [41] (S. Maisel). Our simulations allowed us to determine the transformation temperature as a function of particle size and matrix composition. This was crucial for our experimental colleagues (C. Tasan, MIT Boston), enabling them to optimize the microstructure. In another large scale simulation project we investigated the migration of general (twist and tilt component) grain boundaries [42] and [43] (S. Hadian). We could show that general grain boundaries relax into nano-facets and that their migration is determined by the nucleation and flow of steps (Fig. 7(a)). Based on a new detection method (Fig. 7(b)), we were able to break down the complex migration process into the elementary events (Fig. 7 (c)). Based on this we could set up a kinetic Monte Carlo simulation in order to access experimental time scales. Within this work, we also developed a software package that enables an easy to handle construction of general grain boundaries [44].

Several further method developments and investigations have been pursued in the group. We have developed a quantum mechanical/molecular
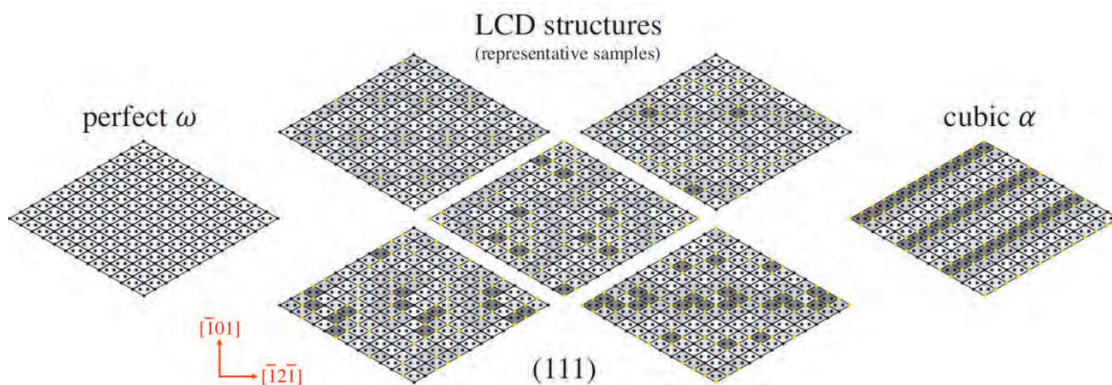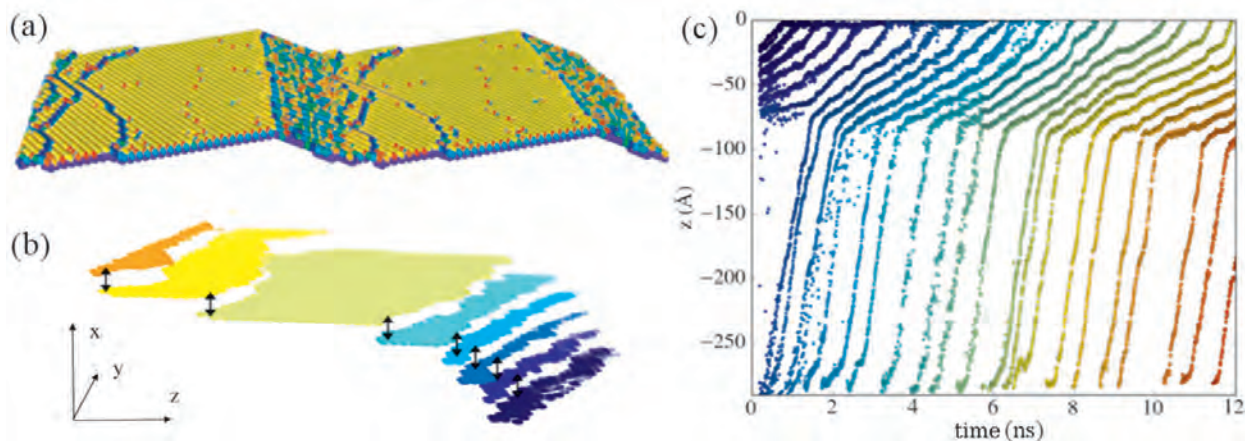

Fig. 6: *Representative examples of complex atomic structures discovered in Ti by finite temperature ab initio MD.*

Fig. 7: *Molecular dynamics simulations of a general grain boundary (in the vicinity of a <111> Σ7 tilt boundary) in aluminum: (a) Snapshots of grain boundary atoms identified by an order parameter. (b) Representation of the grain boundary after applying the newly developed detection method. (c) Propagation of the steps as a function of time.*

mechanical (QM/MM) approach that is easily applicable to structures in which a defect (e.g., grain boundary) passes through the domain [45] (L. Huber). Moving towards larger scales, we also developed a molecular mechanical/finite element method (MM/FEM) coupling scheme (L. Huber; (see p. 71)). In close collaboration with experimental colleagues (B. Gault MA department) we introduced a machine-learning based method to automatically detect atoms from field-ion microscopy data [46].

Complex Concentrated Alloys (F. Körmann)

The key focus of the Complex Concentrated Alloys (CCA) project group is to develop the computational tools to satisfy the ongoing and increasing demands for the computational design and data-driven exploration of complex, multi-component alloys including the recent class of high entropy alloys (HEAs). To achieve this goal, the CCA group focuses in particular on advancing the approaches developed in the CM over the years towards complex multi-component alloys. The CCA group has a strong interdepartmental angle within the MPIE (e.g., via the SPP priority programme) and strongly collaborates with international groups (e.g., the Materials Science and Engineering Department, TU Delft, The Netherlands).

A main part of the simulation activities addresses the recently proposed class of HEAs, i.e. multicomponent solid solutions based on usually four to six main components (see p. 60). The large compositional space spanned by such alloys cannot be captured by experiments alone and *ab initio* techniques have emerged as a powerful complementary approach [47].

A crucial materials property is the mechanical performance. Recently most works on HEAs were based on investigations focusing on single phase solid solutions. In 2016 an alternative approach [48] was proposed based on experimental findings for a dual-phase (DP) HEA consisting of fcc and hcp

phases. The $Co_{10}Cr_{10}Fe_{50}Mn_{30}$ alloy revealed a TRIP effect, as well as enhanced mechanical properties. The key ingredient to design such novel DP multicomponent alloys is to determine the fcc-hcp stability via tuning the alloy composition. This has been achieved in [44] by *ab initio* simulations in combination with thermodynamic concepts. $Co_{20}Cr_{20}Fe_{40-x}Mn_{20}Ni_x$ alloys with x=0-20 at.% were investigated. A critical value of ~6 at.% Ni was identified as a potential TRIP alloy and subsequent experiments validated the predictions. In the SPP 2006 (see p. 60) this direction is currently being extended towards the impact of interstitial impurities such as C or N, which promise enhanced interstitial solid solution strengthening but also impact the fcc-hcp stability and stacking fault energies. Further, the impact of local chemical fluctuations on stacking fault energies is investigated. A recent study combining the supercell approach with the coherent potential approximation revealed a strong impact of such fluctuations on the stacking fault energy. For prototype fcc CrCoNi and FeCoNiCrMn, compositional changes close to the stacking fault can induce variations of up to 100mJ/m², also suggesting a considerable driving force for chemical segregation, e.g., Mn segregation towards the fault plane or Ni depletion near the stacking fault [49].

Since a large class of HEAs and CCAs are magnetic, knowledge about the magnetic ordering in these alloys is crucial. Established approaches based on direct computations of magnetic interaction parameters and subsequent Monte Carlo simulations are computationally demanding and therefore only applicable to a limited set of alloys. The group has therefore developed an analytic mean field based approach utilising the coherent potential approximation and the disordered local moment model to predict magnetic Curie temperatures in a very efficient way [50]. This enabled high-throughput calculations for thousands of alloys and revealed the possibility to tune Curie temperatures by adjusting the composition.

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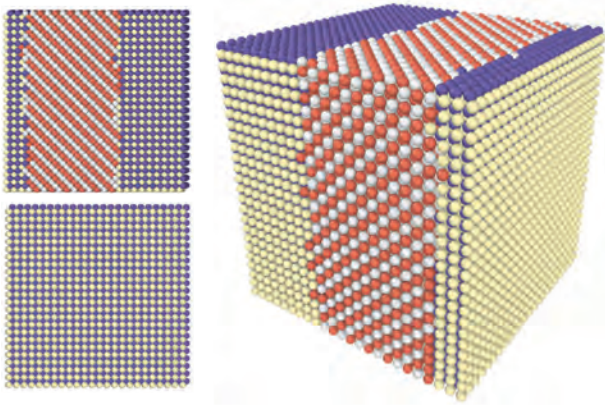
Fig. 8: *Predicted ground state of the bcc NbMoTaW HEA consisting of a B2(Mo;Ta) (blue and yellow) and a B32(Nb;W) (red and silver) decomposition [51].*

Fig. 9: *Temperature dependence of the phonon spectra along <110> direction for (a) $Fe_{72}Pd_{28}$ and (b) $Fe_{72}Pt_{28}$ Invar alloys. Blue and red lines are computed in the fully ordered and disordered magnetic state. The newly developed scheme also allows to compute intermediate temperatures (green lines). The magnetic fluctuations harden the phonon branches, which counteracts the usual thermal expansion and contributes to the Invar effect [55].*

The chemical ordering is another critical ingredient for the design of CCAs. By compositional tuning based on *ab initio* calculations in collaboration with the ASM group, a new type of hcp Al-Hf-Sc-Ti-Zr HEA with an ordered superstructure was designed. This was achieved by tuning the Al concentration towards a $D0_{19}$ ordering on the hexagonal lattice. In general, however, the competing ordered configurations to be considered are not known in advance. At the same time, the established techniques such as cluster expansion quickly approach their limits for multicomponent alloys and require rather crude approximations such as, e.g., the limitation of nearest-neighbour pair interactions. By applying a perturbational approach based on the coherent potential approximation to extract pair interactions for a prototype bcc NbMoTaW HEA (see also Fig. 8) it was shown that the chemical interactions can be very long-ranged and can cause chemically frustrated configurations in the system, eventually stabilizing the solid solution [51]. Later supercell based calculations also revealed that local lattice distortions can further contribute to a stabilization of the alloy [52]. Lattice distortions are one of the so-called core effects of HEAs and were also shown to be significant in other, fcc-based HEAs such as FeCoNiCrMn [53]. The group currently works on extending these concepts by combining explicit supercell calculations with new generation of machine-learning potentials, which are capable of treating multicomponent alloys very efficiently, including the impact of lattice distortions and thermal vibrations.

For simulating lattice vibrations, a number of new tools were developed. In a recent study, *ab initio* calculations for twelve different refractory alloys were performed in combination with the band-unfolding technique to address the question in how far the inherent chemical complexity impacts phonons. The results revealed that both, the atomic mass as well as the force constants significantly contribute to the actual phonon energies and broadening of the

spectral densities. This will enable future research to computationally design the phonon broadening for, e.g., thermoelectric applications, and opens the avenue towards tailored high temperature high entropy alloys.

As many high entropy alloys are magnetic, local magnetic fluctuations can affect other entropic contributions such as vibrations. Here, the group works on advancing the required simulation tools. A major advancement was the extension of the spin-space averaging (SSA) method [54] to magnetic random solid solutions [55]. In [49] a new scheme combining Quantum Monte Carlo simulations, SSA and band-unfolding approach was proposed. The approach was applied to the challenging magnetic Fe-based Invar alloys, for which the cause of their unusual low thermal expansion properties is, after half a century of research, still not fully understood. Based on the new computational scheme it was shown, that magnetic fluctuations strongly contribute to specific phonon branches (see Fig. 9) and thus contribute to the Invar effect [55]. The results reveal the strong interplay of atomic and magnetic fluctuations, which will be a critical factor in further exploring the physics of other complex alloys such as HEAs. An extension towards the inclusion of dynamic spin-lattice effects are currently being explored in collaboration with the

ASM and the CPS groups within the CM department. Application to a prototype CrN alloy revealed [9] a strong impact on phonon, as well as magnon, lifetimes. Currently the extension of such techniques towards more complex alloys is being explored in collaboration with A. Shapeev (Skoltech/ Moscow) by extending recently developed machine-learning potentials towards magnetic systems.

Electrochemistry and Corrosion (M. Todorova)

The Electrochemistry and Corrosion group aims at understanding how **interactions with the environment influence and modify materials and their properties**. With a strong focus on corrosion and, more generally, electrochemical processes the group is continuously extending existing methods, as well as, developing new methods to gain an in-depth atomistic understanding of the physical and chemical processes taking place at surfaces and (solid/ liquid) interfaces. To this end, the group also closely collaborates with different groups at the MPIE, in particular the "Defect Chemistry and Spectroscopy" group (CM) and the "Atomistic Modelling" group (GO).

The employed methodologies are firmly based on *ab initio* calculations. These calculations are often combined with thermodynamic approaches and/ or statistical mechanics enabling their extension to the macroscopic scale. The ensuing ability to compare computational findings with experimental observations is often invaluable, as exemplified for the following case of ZnO surfaces in aqueous environment. While it is generally accepted that knowledge about surface structures forming at solid surfaces immersed in an electrolyte is important to understand processes occurring in electro-chemical environment, little is known about the role the solvent plays towards their formation and stabilisation. The work of S. Yoo addressed this question, building on a methodological framework developed in the group [56,57]. Using two types of density functional theory (DFT) calculations, S. Yoo constructed *ab initio* derived surface Pourbaix diagrams, i.e. diagrams depicting regions of stability of surface reconstructions as a function of applied bias *U* and pH-value of the solution. In one case, the aqueous environment was neglected in the DFT calculations, except for water constituents (O, OH and H) specifically adsorbed on the surface. In this case, the impact of the aqueous environment is accounted for only implicitly by the thermodynamic model used to construct the surface Pourbaix diagram (Fig. 10, left). In a second set of calculations, the aqueous environment was explicitly included in the DFT calculations for the same set of surface structures. The effect of the aqueous environment is therefore explicitly accounted for in the resulting surface Pourbaix diagram (Fig. 10, middle). Comparison to experiments by M. Valtiner (GO) revealed that only the diagram constructed from DFT calculations with the explicitly included aqueous environment reproduces the experimental observations. The ensuing careful analysis of the electronic structure calculations revealed that solvation effects are highly selective. They revealed that due to the high propensity of metallic surfaces for screening unfavourable electrostatic interactions, solvation has little effect on surfaces with metallic character. In contrast, surfaces with semiconducting character, in particular those hampered by a high electrostatic
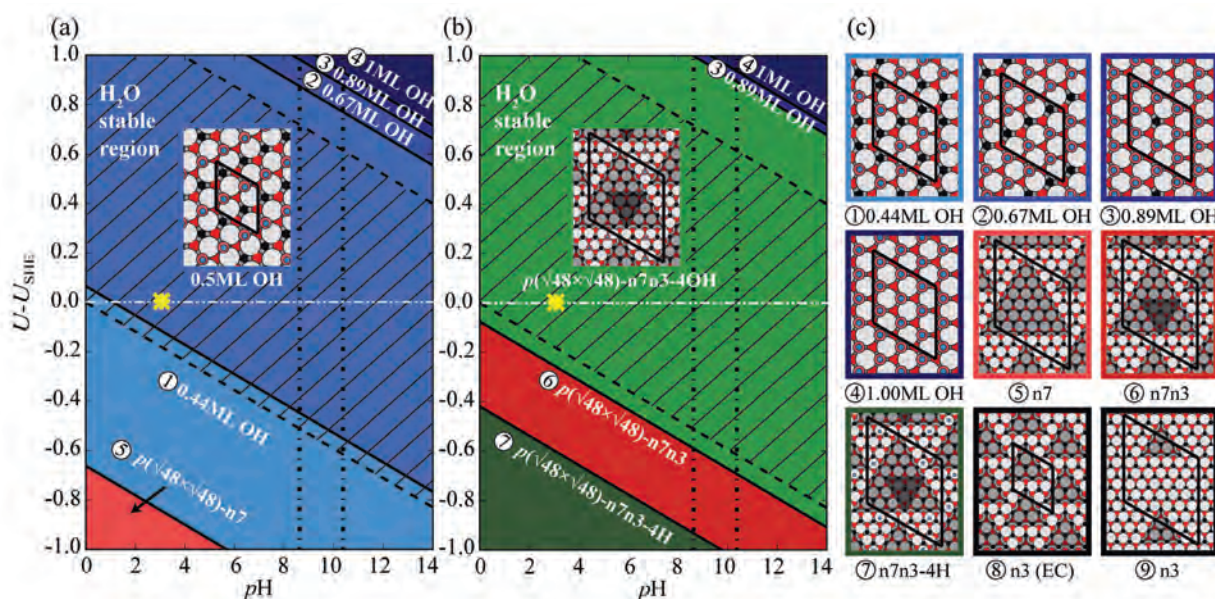
Fig. 10: *Surface Pourbaix diagram for the ZnO(0001) surface constructed using DFT calculations in which the aqueous environment (left) is not explicitly included and (middle) explicitly included in the calculations. The various surface reconstructions appearing in the phase diagram are shown as insets or to the right. The conditions at which a triangular surface reconstruction is observed experimentally are marked by a yellow star.*

penalty in vacuum, experience a strong stabilisation by the solvent and a high gain in solvation energy. This work was highlighted as an "Editors' suggestion" in Physical Review Letters [58].

Staying with the topic of stability of solid surface in contact with a liquid, the work of A. K. Vatti addressed the questions how ions other than H^+ or OH^- affect the stability of surface reconstructions. Looking at clean and solvated Muscovite Mica (0001) surfaces, he was able to connect the surface stability to relevant K^+ ion concentrations, as well as explain the experimental observation of mica surfaces swelling in contact with water but not when immersed in ionic liquid [59].

A significant breakthrough in the modelling of electrochemical surfaces under realistic conditions is **the development of an "*ab initio* potentiostat"**, which enables *ab initio* calculations at solid/liquid interfaces under applied bias (S. Surendralal). Details about the method and the new insights it provided into the anomalous hydrogen evolution at anodically polarised magnesium surface in aqueous environment [60] are discussed on p. 199 .

Corroding surfaces may become amorphous. To address the question what are characteristic features of an **amorphous surface** and how do we build up representative models accessible to electronic structure calculations, which enable meaningful conclusions, M. Tautschnig recently ventured into the area of amorphous solids. Further activities in the group aim at understanding other fundamental properties of investigated materials, which affect their behaviour in solution or the correct way to model them. Examples are the (internal) polarisation of compound semiconductors (e.g. ZnO) or the energy level alignment (i.e. the relative position of energy levels with respect to each other), which become crucial in the context of surface reconstructions or reactions occurring at the interface.

To facilitate discussions with colleagues and aid these developments, the group is also active in co-organising international meetings, like the "High electric fields in electrochemistry and in atom probe tomography" workshop in March 2017.

### Defect Chemistry and Spectroscopy (C. Freysoldt)

The group "Defect Chemistry and Spectroscopy" 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 semiconducting 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 [61]. Interestingly, the methodological developments of the past years have opened opportunities for new applications, notably in the area of **electrified-surface simulations**. Electrified surfaces carry a finite charge and are therefore associated with macroscopic electric fields. Understanding the location of the charge at the atomic scale and the impact of the fields on the energy landscape, geometry, and electronic structure of the surface is of great interest not only in electronic devices - that originally motivated the methodological efforts, - but also for electrochemistry (see p. 47), atom probe tomography (APT) and field ion microscopy (FIM). This gives **unique opportunities to generate novel theoretical insights into APT and FIM experiments** carried out in the MA department (B. Gault), and to improve their evaluation and interpretation.

The development of the multi-scale programme package SPHInX [5,62] is a continuous activity of the group. In addition to further improvements of the parallelization efficiency, recent in-house developments cover a novel geometry optimization scheme [63], Hubbard-U corrections for molecular orbitals [64], and a generalized dipole correction to account for surface calculations with large fields. An important aspect is making use of SPHInX in the pyiron framework and other simulation tools. For this, a pipe-based interface and a communication protocol was developed to control the program flow by external tools. For instance, the unique spin-constraint capabilities (M. Grabowski) of SPHInX have been used to rapidly devise spin-space algorithms in the Computational Phase Studies (T. Hickel) group, without the need to train scientists in DFT code development. Reversely, based on the same protocol, the new **powerful SPHInX geometry optimizer** [63] is made available to other programs. Both workflows have been successfully integrated into the pyiron framework. Extending the protocol to further features will accelerate the rapid prototyping of complex simulation protocols across traditional code boundaries beyond the current paradigm of generating input files and restarting the DFT code for each step.

The role of electrostatics for atomic-scale simulations at surfaces is of high interest for us. Surfaces are typically modelled in the repeated slab approach: the bulk material below the surface of interest is truncated, and – in order to take advantage of the highly efficient computer codes available for bulk crystalline materials – periodic boundary conditions are applied (with a certain amount of vacuum between the slabs). However, surface charges modify the macroscopic field along the surface normal, and hence are incompatible with periodic boundary conditions. Therefore, all such calculations contain implicit or explicit compensation charges, leading to artefacts in the field distribution and the energy. Much care is required to transfer raw simulation results to experimentally relevant situations. One approach is to produce more
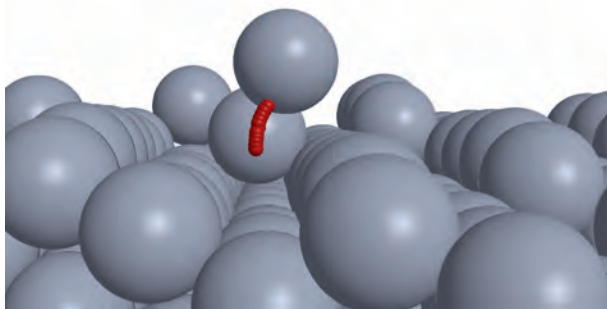
Fig. 11: *Field evaporation from a kinked Al surface: the trajectory (small red spheres) of the evaporating atom shows roll-over instead of a straight path due to bonding to neighbour atoms.*

realistic field distribution. For uncharged slabs with a permanent dipole, this is common practice: the "dipole correction" adjusts the potential in the vacuum to account for the vacuum potential shift induced by the slab's dipole, and avoid an artificial compensating field. For charged slabs, we generalized the dipole correction to adjust the field and the potential.

This new scheme enables us to address the **details of field evaporation and field-ion microscopy** by means of DFT calculations (A. Mishra, M. Ashton). This is driven by a collaboration with the experimental APT group (B. Gault) at the MPIE, and embedded in the BigMax network (see p. 53). DFT calculations for the elementary evaporation process yield not only element- and site-specific critical fields and barriers, but also show the source of trajectory aberrations by the roll-over effect, see Fig. 11. They also serve as input for meso-scale simulations of tip evolution (M. Ashton), which are required to develop and gauge improved reconstruction algorithms for APT.

In contrast to high-field applications, charges at semiconductor and insulator surfaces typically localize at surface defects at much lower densities than what can be feasibly simulated. In this case, correcting for the artificially high fields is the better choice. Along the lines of the Freysoldt-Neugebauer-van-de-Walle scheme for bulk defects, we had developed a preliminary correction scheme already in the previous reporting period. In this period, the scheme was further improved to also yield the field-dependence of formation energies and has now been finalized, published [65], and made available to the scientific community [5]. Ongoing work focuses on application of the scheme to **defects in 2D materials** in collaboration with R. Hennig (University of Florida, USA).

The modelling of disorder is another interest. Within a collaboration with the Max-Planck institutes for Solid State Research (Stuttgart) and for Chemical Physics of Solids (Dresden), we studied charge ordering in potassium sesquioxide (K_4O_6). This compound had evaded synthesis attempts for decades, but was recently realized by our experimental collaborators from a surprising disordered precursor

that forms in equilibrium at elevated temperatures. The modelling of sesquioxides is challenging due to the presence of π-electron correlations between O_2 building blocks and the associated structural relaxation, giving rise to dynamic polaron hopping between distinguishable -2 and -1 molecular charge states. The DFT predictions using the newly developed Hubbard-U corrections for molecular orbitals, which are essential to include π-electron correlations in an efficient way, show excellent agreement with experimental results. The compound's thermodynamic stability was found to originate from polaron entropy as a novel stabilization mechanism, which may open a new understanding of mixed-valence compounds that exist, for instance, also in corrosion layers [64].

Disorder exists also in CuCr bcc alloys produced by molecular beam epitaxy. Cu does not usually exist in the bcc phase, but may precipitate from bcc alloys in the form of nanoparticles which are difficult to analyse. It is therefore of high interest to understand spectroscopic signatures from larger samples. In collaboration with C. Liebscher (SN), we simulated the electron-energy loss spectra (EELS) of Cu-Cr bcc alloys [66]. According to the calculations, random alloys show a clear composition-dependent feature in the Cu L_{23} edge. Experiments for Cu-rich alloy (67%) showed the feature not at the expected position for the average composition, but at much higher Cu content. This is indicative of demixing at the nanoscale, in agreement with strong composition fluctuations detected by STEM.

Growth Modelling (L. Lymperakis)

The growth modelling project group investigates the **epitaxial growth and the properties of compound semiconductors and nanostructures**. The research interests of the group focus on the thermodynamics and kinetics of epitaxial growth, the electronic properties and energetics of surfaces and interfaces as well as the growth and the properties of semiconductor nanostructures. Within the reporting period L. Lymperakis was and is involved in one EU and BMBF co-funded project (PowerBase) and in one DAAD (Deutscher Akademischer Austauschdienst) funded project **(Superlattices of ultrathin InGaN/ GaN quantum wells for advanced optoelectronics and topological insulator applications, ULTIMAT)**.

Topics that were and are addressed by the growth modelling group include, but are not limited to:

III-Nitride alloys such as InN, GaN, and AlN dominate the optoelectronics industry with applications in light emitting devices (LED), laser diodes (LD), and power electronics. The growth, as well as the bulk and surface thermodynamics of InGaN alloys were investigated in collaboration with the Defect Chemistry and Spectroscopy group (C. Freysoldt) and the Institute for Crystal Growth in Berlin (M.
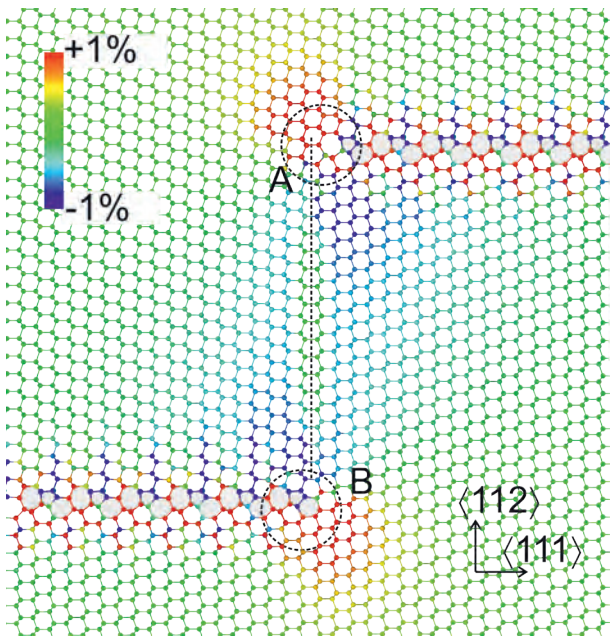
Fig. 12: *Local atomic strain at a Σ3{111} twin segment in Si (dashed line) embedded between two asymmetric Σ3{112} facets. The dashed circles denoted as A and B indicate the two junction cores. Blue and red regions denote compressive and tensile strain, respectively [72].*

Albrecht). An exhaustive ground-state search using DFT calculations was employed to set up a Cluster-Expansion (CE) Hamiltonian, which was used to perform canonical and grand canonical Monte Carlo simulations. The derived phase diagram of bulk In-GaN alloys biaxially strained to GaN exhibits a rich set of hitherto unknown chemically ordered phases at various stoichiometries, in contrast to the wide-held belief that these alloys can be described by a simple regular solution model with a large miscibility gap.

A possible route to overcome key challenges related to high quality and high In content InGaN alloys is to employ **surface engineering**, i.e. to employ surface structures with compositions higher than the bulk solubility limit which are kinetically stable and do not change their composition when overgrown. We addressed this concept by combining *ab initio* simulations with advanced experimental characterization techniques (molecular beam epitaxy, MBE, high resolution transmission electron microscopy, HRTEM, and reflection high-energy electron diffraction, RHEED) to investigate the growth of single monolayer InGaN/GaN superlattices (SL). Specifically, we showed that the growth of the optically active InGaN films is self-limited with respect to thickness and chemical composition. Our calculations reveal that the **origin of the self-limitation is a novel surface stabilization mechanism**, elastically frustrated rehybridization [67]. In contrast to present understanding of surface stabilization mechanisms based on bond strength optimization, this mechanism prevents In atoms from occupying low-coordinated surface sites. The surface energetics indicate that this mechanism

imposes strict upper limits in the order of 25% on the maximum In content that can be achieved at the surfaces. The new insight allows to surface-engineer growth to achieve alloys with contents that exceed the bulk solubility limits. Indeed, in a recent study we showed that surface rehybridization provides promising routes to grow B containing ternary nitride alloys with B contents exceeding the bulk solubility limits by almost one order of magnitude [68].

A common impurity, which is intentionally or unintentionally present during growth of III-Nitride surfaces, is hydrogen. The electronic and vibrational properties, the thermodynamics and kinetics of molecular and atomic hydrogen adsorption/desorption at/from non-polar GaN surfaces were investigated in a synergetic study with the Technical University of Ilmenau using DFT calculations and ultraviolet (UPS), X-ray (XPS) photoelectron and electron energy loss (EELS) spectroscopy experiments. Our results revealed that chemisorption in a gas exposure experiment is strongly dependent on the experimental conditions as well as on the energetics and kinetics of the dissociation/ adsorption reactions at the surface. In a series of ***ab initio* designed and driven experiments** we could confirm that hydrogen desorption requires elevated temperatures and is predominantly taking place as hydrogen molecules are desorbing from surface dimers [69].

Other topics related to the growth and properties of III-Nitride surfaces and nanostructures that have been addressed in the reporting period include the investigation of the electronic properties of non-polar AlInN(10$\underline{1}$0) surfaces [70] in collaboration with cross sectional scanning tunneling spectroscopy (Peter Grünberg Institut at Forschungszentrum Jülich), the selective-area growth of GaN nanowires on masked substrates (in collaboration with MBE experiments, Department of Physics, University of Crete, Greece) [71], as well as the energetics and electronic properties of fluorination of clean and oxidized GaN surfaces in collaboration with Infineon Technologies Austria AG. Fluorine adsorption and incorporation is employed to investigate and understand the electronic properties of the dielectric-barrier interface of metal-insulator-semiconductor high electron mobility transistor (MIS-HEMTs). The calculations revealed a strong tendency of fluorine to passivate cation dangling bonds even under extreme fluorine-poor conditions. Moreover, fluorine passivation induces considerable changes to the electronic properties of the surfaces/interfaces: Passivation of surfaces with oxide stoichiometry removes states from the gap. Nevertheless, passivation of surfaces that obey the electron counting rule shifts the surface states deeper into the gap.

The energetics as well as atomistic mechanisms underlying the **segregation of impurities at Si grain boundaries (GB) and GB junctions** were investigated in collaboration with the MA and SN departments

THE DEPARTMENTS

in a PhD project (M. Alam). Here, we employed DFT calculations to parametrize Si, C and Si-C modified embedded atom method (MEAM) interatomic potentials. Careful benchmarks showed that these potentials provide an accurate description of the atomic geometry, strain, and energetics of intrinsic Si GBs as well as of the C segregation at the aforementioned interfaces. Based on this new potential, we identified the preferential carbon segregation at faceted GBs at the experimentally relevant length scale. Using this insight, we were able to interpret the experimental findings showing an asymmetric line segregation of impurities along one particular type of facet junction core, instead of a homogeneous decoration of the facet planes. More specific, we showed that this **asymmetric segregation pattern** is a consequence of the interplay between the atomic arrangements at the core structure of the facet junction and the corresponding local strain state [72].

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Research Projects in Progress

Collaborative projects involving several groups

Janßen, Surendralal, Huber, Waseda, Hickel, Grabowski, Todorova, Feysoldt, Neugebauer (in collaboration with Y. Lysogorski* and R. Drautz*, *ICAMS): Development of the pyiron platform

Zhang, Grabowski, Hickel, Körmann, Neugebauer (in collaboration with Y. Gong* and R. Reed*, *University of Oxford, UK): Temperature dependent stacking-fault-energies in Al, Cu, and Ni from ab initio

Stockem, Grabowski, Hickel, Körmann, Neugebauer (in collaboration with B. Alling*, *Linköping University, Sweden): Coupling of spin fluctuations and lattice vibrations

Grabowski, Hickel, Neugebauer (in collaboration with A. Glensk*, P. Neibecker** and M. Leitner** (*EPFL, Switzerland, **Technical University München)): Accurate determination of phonon linewidths

Grabowski, Körmann, Zhang (in collaboration with L. Rogal*, *Polish Academy of Sciences Krakow, Poland): Development of hcp based high entropy alloys

Ishibashi, Grabowski, Körmann: Thermo-dynamics of metastable Ti fcc

Grabowski, Freysoldt, Ikeda, Körmann (in collaboration with A. Shapeev*, A. Duff** (* Skolkovo Institute of Science and Technology, Russia, **Daresbury Laboratory, UK): Machine-learning potentials for computing anharmonic free energies of VMoNbTaW high entropy alloys

Ikeda, Grabowski, Körmann, Neugebauer (in collaboration with S. Ishibashi*, *AIST, Japan): Concept of atomic pressure and lattice distortions to characterize mechanical performance of bcc refractory high entropy alloys

Körmann, Hickel, Neugebauer (in collaboration with N. Wang*, T. Hammerschmidt*, R. Drautz*, *ICAMS, Bochum): Ab initio simulation of magnetic contributions to the thermodynamics of metals

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

Adaptive Structural Materials (B. Grabowski)

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

Hadian, Grabowski, Neugebauer: Molecular dynamics simulations of grain boundary migration

Hadian, Grabowski, Neugebauer: Development of a coincident site lattice software package for easy grain boundary creation

Huber, Grabowski, Neugebauer: Molecular mechanics/finite element method coupling

Zhang, Grabowski (in collaboration with S. Divinski*, *University Münster): Diffusion in high entropy alloys

Huber, Dsouza, Grabowski: Temperature dependent free energy barriers

Grabowski (in collaboration with A. Forslund* and A. Ruban*, *KTH Stockholm, Sweden): Anharmonic free energy calculations in TiN

Grabowski (in collaboration with F. Mouhib*, J. Guenole*, S. Korte-Kerzel*, *RWTH Aachen): Synchroshear mechanism in Laves phases

Complex Concentrated Alloys (F. Körmann)

Ikeda, Körmann, Neugebauer (in collaboration with X. Wu*, Z. Li*, D. Raabe*, *MA Department): Impact of interstitial alloying on stacking fault energies in FeCoNiMnCr high entropy alloys

Ikeda, Körmann, Neugebauer (in collaboration with S. Sohn*, D. Raabe* and S. Ishibashi** (*MA Department, **AIST, Japan)): Relation of local lattice distortions and atomic pressure on strength of VCoNi alloys

Körmann, Neugebauer (in collaboration with B. Dutta* and A. Shapeev** (*TU Delft, The Netherlands, **Skolkovo Institute of Science and Technology, Russia)): Development and application of machine learning potentials for magnetic systems

Körmann (in collaboration with B. Dutta*, *TU Delft, The Netherlands): Exploring $(Mn,Fe)_2(P,Si)$ magnetocaloric materials with ab initio

Körmann (in collaboration with Z. Rao*, Z. Li*, D. Raabe* and B. Dutta** (*MA Department, **TU Delft, The Netherlands)): Tuning magnetic properties and Curie temperatures in high entropy alloys

Körmann, Neugebauer (in collaboration with A. Shapeev*, *Skolkovo Institute of Science and Technology, Russia): Machine-learning potentials for exploring the phase stability and configurational ordering in MoNbTaW high entropy alloys

Computational Phase Studies (T. Hickel)

Aslam, Waseda, Hickel: Improving empirical potentials by machine-learning techniques

Chakraborty, Hickel, Neugebauer (in collaboration with B. Gault*, *MA department): Hydrogen in aluminum alloys

Gajera, Janßen, Hickel, Neugebauer: Automatized determination of phase diagrams based on empirical potentials

Gupta, Hickel (in collaboration with B. Dutta, S. Divinski** and G. Wilde** (*TU Delf, The Netherlands, **Universität Münster)): Mechano-chemical coupling during precipitate formation in Al-based alloys*

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

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

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

Lochner, Hickel (in collaboration with I. Eremin, *Ruhr University Bochum): Ab simulation of electronic and structural properties of iron-based superconductors*

McEniry, Tehranchi, 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*

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

Sözen, Hickel, Neugebauer (in collaboration with O. Gutfleisch, S. Biermann**, L. Pourovskii** (*TU Darmstadt, **Ecole Polytechnique, Paris, France)): Rare-earth-based alloys for hard magnetic applications: Temperature and pressure dependent phase stabilities*

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

Tehranchi, Hickel, Neugebauer (in collaboration with C. Hüter, R. Spatschek*, *FZ Jülich): Ab initio based mesoscale simulation of hydrogen embrittlement*

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

Defect Chemistry and Spectroscopy (C. Freysoldt)

Ashton, Freysoldt, Neugebauer (in collaboration with B. Gault, *MA department): Machine-learning for reconstruction of atom-probe tomography data sets*

Ashton, Freysoldt. Neugebauer: DFT calculations of field evaporation from metal surfaces

Freysoldt, Ashton, Neugebauer (in collaboration with S. Katnagallu, I. Mouton*, L. Stevenson*, B. Gault*, D. Raabe*, *MA department): DFT calculations for Field Ion Microscopy*

Freysoldt, Neugebauer (in collaboration with C. Liebscher, A. Ziletti**, L. Ghiringhelli**, (*SN department, **Fritz-Haber-Institut, Berlin)): Automatic classification and feature extraction from multi-dimensional STEM data*

Freysoldt, Waseda, Janßen: Method development across code boundaries via pipe-based inter-code communication protocols

Electrochemistry and Corrosion (M. Todorova)

Yoo, Todorova, Neugebauer (in collaboration with D. Marx, *Ruhr-University Bochum): Impact of oxygen vacancies on Au nanoclusters supported on $TiO_2(110)$.*

Yoo, Todorova, Neugebauer (in collaboration with C.G. Van de Walle, *University of California, Santa Barbara, CA, USA): Polarisation in semiconducting compounds.*

Surendralal, Todorova, Neugebauer: The platinum-water interface in an electrolytic cell under open circuit conditions and under bias.

Surendralal, Todorova, Neugebauer: De-solvation of Mg-surfaces in aqueous environment

Tautschnig, Todorova, Neugebauer: Stability of low index surfaces of Anorthite in dry and wet/aqueous environment

Tautschnig, Todorova, Neugebauer (in collaboration with Schott AG): Modelling corrosion of glass surfaces

Surendralal, Janßen, Todorova, Neugebauer: VASP in pyiron

Tautschnig, Janßen, Todorova, Neugebauer: Phase diagrams in pyiron

Growth Modelling (L. Lymperakis)

Lymperakis, Neugebauer (in collaboration with T. Schultz, M. Anikeeva*, and M. Albrecht*, *Leibniz Institute for Crystal Growth, Berlin): Recombination in (In,Ga)N quantum structures - role of hole localization.*

Lymperakis (in collaboration with G. Dimitrakopoulos*, A. Georgakilas** and E. Dimakis*** (*Aristotle University, Thessaloniki, Greece, **University of Crete, Heraklion, Greece, ***Helmholtz-Zentrum Dresden-Rossendorf e.V., Dresden)): Superlattices of ultrathin InGaN/GaN quantum wells for advanced optoelectronics and topological insulator applications

Lymperakis, Neugebauer (in collaboration with B. Alling*, *Linköping University, Sweden): Thermodynamics of nitride alloys for piezoelectric applications

Lymperakis, Neugebauer (in collaboration with Ph. Ebert*, *Forschungszentrum Jülich): Electronic properties of non-polar AlGaN surfaces

Lymperakis, Alam, Neugebauer (in collaboration with the MA and SN departments), Thermodynamics of Si Grain Boundaries.

Lymperakis, Neugebauer (in collaboration with Ph. Vennéguès*, *CNRS-CRHEA, Valbonne, France): Si incorporation at AlN surfaces

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 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.

In the last six years 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 provisional head of the department. Also 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. In December 2015 Andreas Erbe was appointed professor of Corrosion and Interface Chemistry at the NTNU Trondheim (Norway) and Karl Mayrhofer was appointed professor of Electrocatalysis at Friedrich-Alexander-Universität Erlangen-Nürnberg as well as director of the Forschungszentrum Jülich GmbH-Helmholtz Institute Erlangen-Nürnberg for Renewable Energy. And in May 2016 Markus Valtiner was appointed professor for Physical Chemistry "Colloid and Interface Science" at the TU Freiberg. The institute was successful, however, in securing the continuation of the corresponding groups by long term consultancy contracts with these group leaders. At the current stage the groups of Andreas Erbe and Karl Mayrhofer will continue at least until middle of 2019. The department is actively participating in various collaborative research efforts with internal and external partners. An important example is the German Research Foundation (DFG) Cluster of Excellence "Ruhr Explores Solvation" (RESOLV),

Research Groups	Scientific Interests	Laboratories
• Atomistic Modelling • Electrocatalysis • Interaction Forces & Functional Materials • Interface Spectroscopy • Corrosion	• Electrochemical Surface Science • Catalysis and Corrosion • Adhesion and Functional Coatings, Surfaces and Interfaces • Fundamental Research on Surface and Coating Related Process Technology	• Chemical Analysis • Clean Room • Co-deposition (PVD, CVD, PLD) • Corrosion Testing • μ-Electrochemistry (SFC) • Kelvin Probes • High-Resolution SAM/ SEM/ EDX/ EBSD • Optical Spectroscopy • Scanning Probe Techniques

Fig. 1: *Research portfolio and expertise.*

Fig. 2: *Part of the GO department 2018.*

which is centred at Ruhr-Universität 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.

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. 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 and also hydrogen originating form corrosion by through-sample detection with high spatial resolution (see p.45).

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

Fundamental research on electrochemical interfaces is a key activity within the GO department as an in depth characterisation of these interfaces or interphases is of indispensable importance for a full mechanistic description of electrochemical processes in the key areas corrosion and electrocatalysis. In the recent years extensive collaborative experimental and theoretical work focussed especially 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 according *ab initio* simulations. 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 and DFT based simulation, the mechanism of the electrochemical oxygen reduction reaction on n-Ge(100) as a model semiconductor has been investigated, providing deep insight into the reaction mechanisms [1-4]. 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]. Details of the transformation mechanism have been revealed by *in situ* IR spectroscopy [5]. During this surface transformation, water is effectively displaced from the interface, the interfacial hydrogen bond network is weakened, and a "hydrophobic gap" of few Å thickness develops [6,7]. Both interfacial desolvation and interfacial IR absorption spectra have been reproduced by *ab initio* molecular dynamics calculations [6]. Details of the desolvation process have been extracted from the IR spectra by a novel analysis technique, combining a transition model with a principle component analysis based spectrum decomposition [7]. These IR results follow a previous study of desolvation by *in situ* ellipsometry, where also a layer of low refractive index at the interface between hydrophobic organic layers and aqueous electrolytes [8].Ongoing activities center around the stabilisation of oxide-free silicon in contact with aqueous solutions, and the extraction of potential dependent IR spectra. A parallel computational project has been carried out in the Atomistic Modelling Group. Extending previous experimental approaches first attempts have been made to derive depth-dependent IR spectra from the inversion of angle dependent internal reflection data [9].

The molecular structure of the electrode/electrolyte interface is essential in electrochemical and natural processes. In the recent years, we started to use force probe experiments as workhorse to directly probe structural forces at solid/liquid interfaces. For instance, electric double layers in static and dynamically changing systems were studied in a close collaboration with the cluster of excellence RESOLV at Ruhr-Universität Bochum. It was e.g. shown how specific ion adsorption can strongly influence charge compensation in the electric double layer on model ceramic surfaces [10]. Also, anion hydration layers were investigated using force probe experiments, and similar effects were observed [11]. Work was also extended into non-aqueous electrolytes such as ionic liquids and battery fluids. Influence of trace molecules on structuring of ionic liquids at electrified and charged interfaces. It was shown how water and other impurities alter the interfacial structuring and charging characteristics of ionic liquids on dielectric surfaces and electrified interfaces, and electric double layer screening in high salt solutions was shown to proceed via an unexpected long-range mechanism [12-15]. This work was very well received and triggered a rethinking of how force probe experiments in IL liquids should be conducted and interpreted, and how charge compensation works in high salt environments, which was recently reviewed [16].

Of increasing importance is our surface science approach for fundamental investigation of electrode surfaces. For this we have developed a novel methodology that allows to fully control not only the potential of electrodes covered by just ultrathin electrolyte layers, but also to measure the full current density-potential correlation (I(U) curves) for electrochemical reactions such as oxygen reduction on that same electrode. This methodology is based on combining Kelvin probe with a hydrogen permeation experiment, which allows for the first time direct measurement of e.g. the oxygen reduction kinetics at the buried interface, first performed and proven to work in a modified Devanathan-Stachurski set-up where at the exit side the potential was measured instead an oxidation current density [17,18] (see p. 116 and p. 45). This approach is denoted by us as the permeation based potentiometry method (ppm).

This is a breakthrough of highest importance for the field. It will allow us

- to measure current-potential (I(U)) curves on electrodes covered by ultrathin electrolyte layers, even down to the submonolayer range (see p. 45)

- to use analytical surface science tools without any restrictions, as well as other spectroscopic techniques such as infrared spectroscopy (without need of attenuated total reflectance)

- to characterize the full electrode, as the electrolyte layer is very thin and controllable, from clusters over monolayers to nanometres

These electrodes are just covered by ultrathin electrolyte layers denoted by us as "electrodes in the dry". The humidity of the environment can be adjusted to different partial pressures of water, thus adjusting the exact thickness of the electrolyte layers. This novel approach enables us to control the structure of the double layer in a so far unimaginable way. For instance, under full potential control electrodes with double layers containing water in the sub-monolayer range can be realized and still the full current-potential dependence for electrochemical reactions such as oxygen reduction can be obtained. For the first time this should make a fully controllable electrode accessible for analytical techniques for in operando investigation without any restrictions, such as surface analytical tools like NAP-XPS and infrared spectroscopy.

In accordance with the importance of the oxygen reduction reaction for the department the main activities of the current research focus on this reaction. So far ORR on "dry" palladium and iron membranes have been investigated.

This novel approach has also great potential in fundamental research on electrocatalysis. For in-

stance, an interfacial descriptor of the electrocatalytic activity for the hydrogen evolution reaction, analogue to the adsorption energy of H_{ad} intermediate, has been identified by measuring the potential change during nitrogen/hydrogen gas change. The derived activity trends give clear indication that the electrocatalytic activity for hydrogen evolution reaction is a consequence of an interplay between metal-hydrogen and metal-water interactions [19].

Many of the research projects allocated in the field of electrochemical sciences are closely related to the DFG-funded Cluster of Excellence RESOLV with the RUB. 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 [20]. Main aim is again to link experimental results to first principles calculations.

Corrosion

The aim of the department is to obtain fundamental insight into corrosion mechanisms with the aim to develop advanced countermeasures.

During the last six years the corrosion research of the department covered a wide range of topics in the areas of aqueous, atmospheric and bio-corrosion processes and their inhibition, covering both fundamental and applied aspects. In the latter mainly microbially influenced corrosion (MIC) by marine sulfate-reducing bacteria was investigated [21], and information on related direct electron transfer processes at the electrode/bacteria interface was obtained [22,23,24]. One important focus of work on aqueous corrosion was transpassivity. A combination of Raman, PL and ellipsometric *in situ* spectroscopy was used to study surface changes on copper and manganese, initially while forming surface oxides, and subsequently when entering the potential range of the oxygen evolution and transpassive dissolution [25-27]. Also understanding the working mechanisms of corrosion inhibitors is of importance. For instance, the same combination of *in situ* techniques, complemented by IR spectroscopy was used to investigate the mechanism of action of the well-known corrosion inhibitor 2-mercaptobenzothiazole (MBT) with copper. As a result it was e.g. shown that in contrast to current literature opinion, MBT can adsorb to oxide-free copper [28,29].

A key technique for corrosion research is the Scanning Flow Cell (SFC). Using the SFC system with downstream analytics such as mass spectroscopy or UV-vis analysis 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 was applied on a wide range of materials including magnesium,

where it provided important insights, including the much disputed negative difference effect [30,31], zinc alloy coatings [32], and noble metal catalysts. 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 [33-37]. 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 [38-41].

The investigations by SFC are mainly focused on the fundamental active dissolution kinetics. Atmosphere change experiments in the Kelvin Probe, on the other hand, are providing information primarily about the reactivity of the surface oxides of the as prepared samples and to some extent the initial stages of long term performance, depending on the exact exposure conditions and the duration of the experiments. One example is the performance of zinc alloy coatings. The effect of changes from oxygen free to oxygen containing atmospheres and back on the potential measured by Kelvin probe on the surface of such a coating are taken as an indicator for the reactivity of the corresponding surface oxide, which was indeed found to correlate well with observed corrosion behaviour. The potentials obtained by standard Kelvin Probe are averaged over a macroscopic scale of a several thousands of square micrometres, which is much larger than the underlying microstructure. For this reason high resolution studies by Scanning Kelvin Probe Force Microscopy (SKPFM) play a crucial role in unravelling the origin of the observed potential changes. We are currently trying to establish according measurement routines that are expected to make Kelvin Probe based techniques for corrosion research of similar importance as they have already gained for the investigation of coating performance or hydrogen detection. Many problems have to be solved and are addressed in our activities in further developing the Scanning Kelvin Probe methodology (see p. 45). This includes research on how to obtain reliable calibration of potentials measured by Kelvin Probe under different atmospheric conditions [42] as well as how to achieve calibration in SKPFM. Longterm corrosion performance is mainly determined by the corrosion product layers forming over time. These were in focus of research, too, from initial stages to long term. Important information on the effect of environmental factors and the role of

the micro-structure could be elaborated [43-46] and is still ongoing research (see p. 116).

Within the reporting period work was performed to adapt also the surface force apparatus (SFA) for fundamental investigation of corrosion in confined zones. For this, the electrochemical surface forces apparatus, developed partly at the MPIE, was modified to utilize white light interferometry (WLI) for a direct visualization of corrosion processes in real-time, *in situ* in confined (i.e. buried) geometries [47]. This is a unique experiment that allows to *in situ* study e.g. of crevice corrosion (CC) with unprecedented resolution in time and space. In a first case study, we investigated in detail how pure aluminium corrodes in crevice geometries and how vanadate ions can effectively inhibit CC of aluminium [48]. This work was then extended into studying Nickel and its alloys that are prone to CC [47]. This work confirmed at the nanoscale that there is a strong interplay between migration kinetics of chlorides, bulk chloride concentrations, and the related IR drop (voltage drop), which leads to pronounced qualitative changes in the location (at the rim or center) at which pits form, and their subsequent kinetics. Importantly, local fast corrosion was found to play a crucial role in the initial development of a crevice corrosion site within the crevice that drives local pit growth and propagation, suggesting that understanding and controlling surface chemistry, surface defects and morphology are essential to prevent the onset of corrosion in the tested systems. With the EC-SFA it was also possible to uniquely measure local pit-current densities ranging from ≥ 5 A/cm^2 for swiftly arresting noncritical pits, and ~25 A/cm^2 for critical pits. This constituted the first *in situ* and real-time measurement of a local current density of a single corroding pit site with nanometer resolution [47].

High temperature oxidation is another topic that is investigated 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 [49] 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. A more recent example is the investigation of selective oxidation at grain boundaries in noble metal anti-adhesion coatings applied on hard metal molds for hot stamping of high precision glass lenses. Indications for an interaction between chromium stemming from the interlayer between the

anti-adhesion layer and the hard metal and oxygen was found that promotes chromium segregation at the GBs below the stage where oxidation occurs (see [50,51], and p. 56). Such interactions may play also an important role in enhanced grain boundary oxidation phenomena observed e.g. during cooling of certain hot rolled steel grades, which is object of current research.

Adhesion, thin films and friction

Organic coatings play an important role in the research within the GO. One important aspect is understanding coating adhesion. Unravelling the complexity of modern adhesives acting in the macroscopic world relies on understanding the scaling of single molecular interactions towards integral macroscopic interactions. A new and unique approach was developed to demonstrate how it is possible to directly extrapolate a macroscopic work of adhesion based on single molecule Atomic Force Microscopy (SM-AFM) measurements [52,53]. Utilizing specifically end-functionalized poly-ethylenglycol (PEG) tethers extending from lipid bilayers (PEGylated bilayers) and SAM covered AFM tips as model system, dynamic forces-versus-distance characteristics of unbinding a specifically bound single tethered functionality from an apposing chemically well-defined surface were measured. Using non-equilibrium thermodynamics it was then possible to extract equilibrium interaction free energies ($\Delta G0$) from non-equilibrium single molecule adhesion measurements, together with dynamic free energy landscape parameters such as transition state barrier heights and rates of desorption. However, there are significant issues concerning reliability, as it was found that certain arrangements work excellent while others are not useful [54], in a sense that data cannot reliably be converged in the analysis.

Functional surfaces, interfaces and coatings

Our research on coatings is mainly focused on understanding their corrosion driven degradation and how to improve their performance. 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. In this delamination mode oxygen reduction at the buried interface and especially the radicals produced as intermediates or side products play a crucial role in destroying the adhesion at the interface. In order to improve the delamination resistance the standard strategy is to use pretreatments prior to application of the organic coating that effectively inhibit electron transfer reactions at the interface and thus also oxygen reduction. Examples are chromatation and phosphatation, where the first is more or less fully banned now and on the latter there is strong pressure to replace or even skip it. GO is involved in corresponding research. The main

problem, however, is that any development of novel pre-treatments and coating concept is slowed down by the required long term evaluations. Unfortunately, up to now no real break-through has been made in a simulation of the delamination process and long-term prognosis. An important requirement for such simulation is of course a deep insight into the underlying mechanisms and knowledge about the key processes. Hence, for this fundamental investigations of the interfacial (electrochemical-)reactions at buried interfaces are of utmost importance and are hence a key research topic within the department. Further efforts have been made towards understanding details of chemical processes during cathodic delamination through preparation of model polymer systems and an investigation of their delamination rates. For instance, thin polyacrylate films had been prepared on zinc by a co-polymerisation in the presence of zinc surface-modified with covalently bound vinyl-terminated silanes, and their delamination behaviour was studied [55-57] . Also surface bound polymers on iron were prepared by surface initiated atom transfer radical polymerisation. In these polymers, the initiator precursor state is crucial for the final delamination rate [58]. An interesting side observation in these studies was the detection of chemical oscillations and pattern formation during cathodic delamination [59,60].

Up to now one unsolved hindrance for a detailed study of cathodic delamination was that the oxygen reduction rate at the buried interface was not directly accessible. Based on the new methodology of 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. 45). 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 [61]. This also affects 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 [62].

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. We have a leading expertise about the problems involved with the use of conducting polymers for corrosion protection which we have analysed in depth and solutions how to solve them were developed. One main success in the last six years 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 [63,64]. Another major break-through was the suc-

cessful combination of an intelligent organic coating containing smart capsules loaded with monomer with a zinc coating containing capsules that were loaded with a catalyst [65]. For the first time a coating system could be demonstrated to case-sensitively release active agents upon onset of corrosion that closed a macroscopic defects site by formation of a new polymer coating.

A general problem with these intelligent self-healing coatings, however, is that the release of active self-healing agents towards the defect is a limiting factor concerning the time to self-healing and the maximum size of the defect that can still be healed. We have found that this can be only improved by ensuring a much faster release rate. Hence, an important research topic was the effect of trigger signal spreading and mobility of the released active agents on the overall self-healing performance. This work was carried out mainly within the framework of SPP "Self-Healing Materials" funded by the DFG. It is found that the performance indeed can be significantly improved by especially enhancing the trigger signal spreading (see below).

Industrial processes

The expertise of the department is of great relevance for the investigation of fundamental aspects of industrial processes. Especially noteworthy is the potential of the SFC for fast through-put measurement. For instance it can be applied to increase our understanding of the impact of the electrolyte components on the fundamental corrosion mechanism and kinetics of Zn based systems [32]. 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 in the collaborations with industry, 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 time-frame. The SFC has been shown to reliably acquire the activity and the stability of noble metal catalysts with high-throughput [66], and is currently employed for a wide range of different types of porous materials including exciting non-noble catalysts for oxygen reduction [67].

Also work on conversion coatings, e.g on high-strength steels [68,69] and Al-SI coated steels [70], as well as on nanoceramic coatings was carried out. In collaboration with a pretreatment manufacturer different *in situ* spectroscopic techniques have been used to study the effect of cathodic polarisation, such as experienced during cathodic electrodeposition coating, on the structure of a nanoceramic, ZrO_2-based conversion coating on several industrially relevant substrates. No significant structural changes after po-

larisation were found [71]. These conversion coatings have earlier been shown to work by passivating grain boundaries and cathodic intermetallic particles [72].

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 aluminium alloys is being investigated. The department is here mainly involved with chemical and electrochemical surface treatment and *ex situ* investigation of prepared structures [73,74]. Current research mainly focusses on the potential of metallic coatings for enhancing the joining process.

Using a systematic variation of alloy composition and *in situ* spectroscopic analysis has advanced the understanding of sour gas corrosion, the corrosion of steels in the presence of H_2S [75], in a joint project with a steel manufacturer. *In situ* Raman spectroscopy showed the phase evolution of oxide- and sulfide-containing corrosion products in different drying stages [76]. On the example of a Mo-containing model alloy, the interrelation was explored of long term integral corrosion rate as measured by mass loss, and the instantaneous corrosion rate measured by electrochemical experiments [77]. State of the art in this field was also summarised in a book chapter presenting an overview over sour gas corrosion [78].

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 and many of the current activities on these topics are based on that earlier work. A high performing high temperature lab is available for fundamental investigations of according industrial processes [79,80], where also our NAP-XPs might be of interest [49].

Scientific Groups

Electrocatalysis (K. J. J. Mayrhofer)

The research interests of the electrocatalysis group 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 is 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 time-resolved reaction product determination.

The new electrochemical methods, which have been developed in the group over the last years [81] 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 and Differential Electrochemical Mass Spectrometry [82] 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 [83]. The overall performance including selectivity and also stability, as operation over extended times, is crucial for the success of fuel cells and electrolysers, and is investigated [33-35,38-41,84,85]. 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 [86]. 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. The full potential of our combinatorial approach in resolving complex scientific challenges is enabled when electrochemical screening is combined with material library development, which we perform in a long-standing collaboration with the group of Alfred Ludwig from the RUB [87,88]. Activity-stability studies have been further extended to the investigation of different catalyst materials like the promising Ru and Ir oxides for the OER [89,90]. Exciting insights have been generated that helped to resolve the difference in performance and reaction mechanism of amorphous Ir (hydroxy-)oxides and rutile Ir oxides [91-94]. Moreover, the structural evolution of the near-surface oxide layers of Ir-based catalysts was monitored on the atomic scale utilizing a combined electrochemical atom probe tomography (APT) approach for the first time [95]. Combined with the introduction of the Stability-number as a quantitative

descriptor for dissolution during reactions, the behaviour of several different Ir-perovskite structure could be efficiently assessed, leading to potential pathways for improved electrolysis catalyst development [96].

Besides these studies on rather model like electrode surfaces, we are also highly interested in high surface area catalysts as typically employed in real electrochemical 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 [97]. 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 Ferdi Schüth from the Max-Planck-Institut für Kohlenforschung the concept of "confined space alloying" has been introduced, providing alloy catalysts with unprecedented structural and chemical stability [36,98,99]. Furthermore, in collaboration with the National Institute for Chemistry in Slovenia we have demonstrated the beneficial effect of ordered alloy nanoparticle catalysts as well as specific surface doping [100-102], while with the TU Berlin we could show general performance trends of nanoporous alloys for ORR and OER [103-105]. Also non-noble metal catalysts have been majorly improved in joint efforts with Frederic Jaouen and his team from the University of Montpellier, unravelling the active sites and resolving stability challenges using operando investigation during ORR [106-109]. Significant contributions could be also achieved in understanding particularly stability aspects of non-noble electrocatalysts during hydrogen evolution reaction, important for low-temperature water electrolysis [110-112]. Within MaxNET-Energy a strong collaboration with the group of Graham Hutchings from Cardiff University has been established, addressing selectivity and stability challenges of the electrochemical production of hydrogen peroxide in fuel cells (see p. 54) [113-116]. Besides catalyst material challenges, several fundamental aspects of support material, reactor operation strategy and accelerated degradation testing are in the focus of our research [117-119]. Overall, the parallel and time-resolved study of activity, selectivity and stability in electrocatalysis utilizing our unique portfolio of advanced methodologies has led to major enhancement of the understanding of key reactions for electrochemical energy conversion.

Atomistic Modelling (S. Wippermann)

Since 2013, the Atomistic Modelling group is working in three directions: (i) charge density waves and electron/phonon coupling in one-dimensional electronic systems, (ii) interfaces, defects, optical and electronic properties of complex nanostructured materials, e. g., assemblies of nanoparticles and (iii) development of *ab initio* molecular dynamics techniques with finite electric fields to describe electrode/electrolyte interfaces.

Topic (i) is motivated by the exploration of fundamental excitations in one-dimensional charge density waves with topological properties and how to use them as information carriers in new types of information processing. These activities are embedded into the DFG research group FOR 1700 (http://www.atomicwires.de) (see p. 64) [120-123].

For topic (ii), S. Wippermann was awarded an independent junior research group within the "NanoMatFutur" programme of the German Federal Ministry of Education and Research (BMBF). The group No. 13N12972 received 1.8 Mio € from 01/2014 – 12/2019. Group activities cover topics from optical and electronic properties of individual nanoparticles, surface functionalization and defects to colloidal assembly into nanoparticle solids with targeted properties for solar energy conversion [124-128]. Experimental collaborations exist with the groups of Dmitri Talapin at the University of Chicago (synthesis of nanocrystals and nanocrystal solids, EXAFS) and Gerd Bacher at the University of Duisburg-Essen (single quantum dot absorption spectroscopy and time-resolved photoluminescence). It is hoped to understand in detail (a) nucleation and growth processes of nanocrystals, (b) light-induced charge carrier dynamics in general and multi-exciton generation in particular, (c) anomalous temperature dependences of optical properties that are often observed in nanocrystals and (d) colloidal assembly processes into nanocrystal solids as a function of synthesis conditions (see p. 193).

In the context of topic (iii), insights at the atomistic scale into electrochemical and electrocatalytic processes require robust *ab initio* methods to perform molecular dynamics simulations of interfaces between solid electrodes and liquid electrolytes. The groups of C. Freysoldt, M. Todorova in the department Computational Materials Design (CM) and the group of S. Wippermann are optimally suited to develop the required methods (see p. 47). Further collaborations exist with the groups of Giulia Galli at the University of Chicago and Francois Gygi at the University of Davis. In the Atomistic Modelling group, the Modern Theory of Polarization in conjunction with a basis set of maximally localized Wannier functions is used to apply electric fields in *ab initio* molecular dynamics (MD) simulations for solid/liquid interfaces. A first approach to perform MD simulations at constant electrode potential was implemented into the open source density functional theory package Quantum Espresso. Interfaces between elemental semiconductors, such as, e.g., Si and Ge, with liquid water are employed as model systems for corrosion processes and electrode potential-dependent surface structures. The newly developed methods are validated against spectroelectrochemical experiments

performed in the Interface Spectroscopy group of A. Erbe, (see p. 165).

Interface Spectroscopy (A. Erbe)

Activities in the interface spectroscopy group continued also after the move of the group leader Andreas Erbe to NTNU, the Norwegian University of Science and Technology, Trondheim, Norway. The group has a strong focus on using the combination of different *in situ* and operando spectroscopic techniques, such as IR absorption spectroscopy, Raman spectroscopy, photoluminescence (PL) spectroscopy and spectroscopic ellipsometry, to study fundamentals of corrosion processes [129]. *In situ* techniques were often complemented by the necessary *ex situ* experiments.

A combination of Raman, PL and ellipsometric *in situ* spectroscopy was used to study surface changes on copper and manganese, initially while forming surface oxides, and subsequently when entering the potential range of the oxygen evolution and transpassive dissolution. On copper, the importance of the mixed oxide Cu_4O_3 was realised at intermediate potentials [25]. Interestingly, when polarising copper to more and more positive potentials, onset of the oxygen evolution and breakdown of the oxide film coincides with a sudden appearance of a defect luminescence typically attributed to a singly charged oxygen vacancy in Cu_2O. This observations is a hint that oxides may become unstable towards defect formation above certain potentials, which may trigger oxide breakdown [26]. In buffered chloride solution, oxide breakdown occurs at much lower potentials under formation of soluble copper(II) chloro complexes [27] (see p. 167). The latter result is important for the antibacterial action of copper, which was studied earlier [130]. Within the BMBF-funded cluster project MANGAN, aimed at advancing manganese-based oxygen evolution catalysts, similar experiments were done for manganese. Data interpretation is significantly more challenging in this system, due to the many possible oxidation states and different phases of individual oxides, and is hence still ongoing.

Also research on pretreatments [71,72,70,131] and the working mechanism of inhibitors was carried out, namely MBT [29]. Furthermore, in many repeats, the effect of post-preparation aging on the formation of the inhibitor film was shown to be tremendous, highlighting the importance of appropriate pretreatments [28].

The fruitful, long-lasting collaboration with M. Krzywiecki, Silesian University of Technology, Gliwice, Poland, was extended. In a systematic development of photoemission based analysis approaches detailed insight into electronic structure such as band-bending and defect levels at semiconducting oxide / organic interfaces was obtained. Initially, an approach was developed to analyse angular dependent photoemission data with quantitative depth information at surfaces [132], defect levels were characterised and large stoichiometry deviations detected in thin films of ZnO [133], and morphology – local thermal property correlations were established [133]. Especially the analysis of ZnO defect levels advanced the understanding of previous works on which defects can form in electrochemically grown ZnO [134]. More recently, the degradation was investigated of thin layer of the organic semiconductor copper phthalocyanine (CuPc) [135]. Combining angular dependent x-ray photoelectron spectroscopy and photoemission yield spectroscopy, the band structure across a tin oxide/ CuPc interface was characterised in detail (see Fig. 3). Significant stoichiometry deviations in the tin oxide was found, and a charge transfer across this interface [136]. Depending on transfer conditions, this charge transfer could be completely blocked, creating different electronic structures across chemically nominally identical interfaces [137]. The peculiar behaviour of the tin oxide lead to a detailed follow up study, disentangling defect formation vs. changes in oxidation state of tin [138].

The detailed analysis of interfacial electronic structure was crucial in the understanding of the behaviour of the cyclic oligosaccharide β-cyclodextrin (CD), which acts as corrosion inhibitor against zinc corrosion. β-CD does so by destabilising point defect formation in zinc oxide, hence rendering the oxide mode intrinsic and less defect rich than usually found [139]. β-CD can also function as a carrier for hydrophobic corrosion inhibitors, amongst others MBT, and stop corrosion-driven cathodic delamination of coatings in which such inhibitor-CD complexes were incorporated [140]. Other water-soluble polysaccharides [141] and polypeptides [56] have been deposited on metallic zinc as films of 10s of nm thickness, and delamination rates of deposited model top coating were significantly reduced even though these polymers can easily take up water. Reason for the reduction is presumably a decrease in the ion transport rate along the interface [141].

Following up from previous attempts on zinc to exploit a cathodic delamination for the preparation of nanorods [142] by using delamination, it was found that the resulting rods have different optical properties on both ends, due to their different defect structure. This behaviour offers interesting applications for corrosion processes as synthesis method in nanotechnology [143]. Ongoing activities in a Marie Skłodowska-Curie project investigate the possibility to create peptide-based switchable interfaces on metal or semiconductor surfaces.

In collaboration with Academia Sinica, Taipei, Taiwan, nanofluidic channels have been fabricated on a germanium internal reflection element and have

been used to detect proteins, were the total amount of protein need is only in the femtomolar range [144]. Earlier collaboration work with the same partners included the fabrication of an electrode nanogap, trapping of proteins in this gap, and protein detection with Raman spectroscopy [145].

Corrosion (M. 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. During the last six years three major research projects in the group were carried out in the highly competitive programmes of the Christian Doppler Society (namely the CD lab for Diffusion and Segregation

Fig. 3: *Band structure at tin oxide/CuPc interface.*

during Production of High Strength Steel Sheet) and the collaborative project framework of Fraunhofer Society (FHG) and Max Planck Society (MPG), namely the projects "Active coatings for corrosion protection (ASKORR)" and "Initial wear". All three projects were very successful and had a lasting effect on the group´s research. The CD lab especially initiated our research on hydrogen in metals and ASKORR on intelligent self-healing coatings. Initial Wear (2014-2017) refuelled our interest in selective grain boundary research (see p. 56) that was originally started in the CD lab. In detail the 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*

Fundamental research on coating delamination is of paramount interest for the department. This is, however, very challenging, because coating delamination is extremely complex and the buried interface is difficult to investigate, as it is inaccessible for most analytical tools. A huge breakthrough was the new approach based on a potentiometric measurement of the equilibrium potential of the oxygen reduction and oxidation of hydrogen permeating from the backside of the sample to the buried interfaces, denoted by us as permeation based potentiometric method (ppm). This approach overcomes the main obstacle preventing electrochemical measurements at the buried interface, the high resistance of the organic coating against ionic current that makes a controllable polarization of the interface by standard three electrode set-up impossible. From the hydrogen uptake on the entry side thus a full current-potential relationship curve (I(U)) can be constructed [17,18]. The investigations focus on two sets of samples: one are well defined samples based on inert noble metal, which allow well controllable structuring of the buried interface and integration of functional groups e.g. by use of self-assembled molecular films at the interface [146-149], the others are research in progress first on adapting the methodology also on technically more relevant samples, such as coated iron/steel and zinc. Concerning the latter we could show that one possible way to make them accessible by the ppm approach is to apply thin layers onto a Pd membrane. As long as the investigated current densities remain low, this was found not to violate the prerequisite that really about 100% of the hydrogen formed at the entry side is entering the palladium and permeating through it. For instance 100 nm iron at the exit side do not impede the permeation up to current densities of about 100 µA/cm^2 [18]. But this also shows that it is important to investigate the limits of this approach. The other way that is investigated and seems to be very promising is to adapt the ppm approach directly to e.g. iron samples. In this case not 100% of the hydrogen formed at the entry side is taken up, but the according relation was successfully established and was proven to work even up to much higher current densities than the thin film approach on palladium (see p. 45).

However, studies on delamination at buried interfaces are still extremely challenging, because oxygen reduction causes degradation already at very low current densities, i.e. it is nearly impossible to investigate the one independently of the other. This is one key topic of current and very exciting research, which has already yielded highly interesting results, such as an at least partial re-establishment of interfacial bonding

when polarization is stopped for a while and thus the formation of radicals and the correlated attack by radicals pauses (see p. 68). This will be relevant for understanding delamination under real atmospheric conditions, where e.g. humidity change will cause active/passive transitions at the defect site and hence will also cause phases of ongoing cathodic delamination and according breaks. Concerning the effect of the environmental conditions, an important topic of research was the role of CO_2 on the delamination behaviour. Strong indications were obtained that CO_2 is affecting the interfacial ion migration at the interface organic coating/zinc, the initial step inducing the delamination process. A crucial role of ion migration at the coating/metal interface was up to now not recognized and hence is widely neglected. We will accordingly intensify our research in interfacial ion mobility [61,62], also especially with a focus on the effect of CO_2. The effect of different pre-treatments on the interface with different coatings and their effect on ion mobility was studied in detail for aluminium [61, 62].

2. *Electrochemistry in the "dry"*

Electrodes covered by just ultra-thin electrolyte layers are another important topic within the corrosion group. This is of practical importance e.g. for our fundamental studies on atmospheric corrosion, where we take the potential change upon gas changes as an indicator for their reactivity. But electrodes in the dry are of general importance. Many phenomena in corrosion and electrochemistry are still not well understood. For instance, it is known that oxygen reduction of electrode covered by thin electrolyte layers shows a limiting current that does not increase when the film thickness decreases below about 5 microns. Then the maximum current densities are not any longer determined by diffusion, but by the uptake process at the surface. Typical values that are reached lie in the range of a few mA/cm^2. In experiments where we make use of the ppm technique we could show that this is indeed valid at least even down to the range of 500 nm electrolyte thickness. However, when we investigate ORR on a surface just exposed to high humidity and where the electrolyte layer is in the range of 1 nm we could not find a limiting current density up to about 1000 mA/cm^2, which was our experimental limit. It is an interesting question what exactly makes the difference for the O_2 uptake between 1nm and 500 nm electrolyte layer thickness. This is also interesting when seeing results obtained in the electrocatalysis group with a so-called floating cell set-up, where current densities for ORR of several hundreds of mA/cm^2 are readily obtained. Is the high current density achieved there mainly stemming from the outer, very thin fringes of the 3-phase region at the border of the wetted electrode surface? Another example are differences in the I(U) curves e.g. of ORR on palladium and

iron(oxide) between dry and humid conditions where, however, the thickness of electrolyte layer varies less than 1 nm. On iron (oxide) polarization of the surface additionally leads to partial reduction of the oxide which complicates the investigation of ORR on such electrodes, but which can directly be followed by use of the Near Ambient Pressure – X-ray Photoelectron Spectroscopy (NAP-XPS). The NAP-XPS, combined with attached electrochemical cell and Kelvin Probe, is now gaining increasing importance as investigation tool for our studies of electrodes in the dry. Currently, we are complementing this set-up also with integrated infrared spectroscopy in order to obtain also information about ordering in the water layer.

Quite a number of projects have now been started on the topic of electrodes in the dry, including besides the mentioned research, fundamental investigation of so called "frozen" double layers, where we transfer polarized electrodes e.g. to the Kelvin Probe and the NAP-XPS for characterization. Regarding the hydrogen electrode in the dry on Pd [150] the main focus is currently to understand why the pH remains so stable. This is the reason why the potential measured by Kelvin Probe on Pd in nitrogen atmosphere can be used as a direct measure for the hydrogen content. However, in principle, since the equilibrium reaction is $H_{ab} \leftrightarrow H^{ad} \leftrightarrow H^+ + e^-$ an increase in H in the metal should lead to an increase in H^+ in the nanoscopic layer, because the layer in contrast to bulk electrolyte has no buffering capability. However, the observed behaviour is in accordance only with a pinned pH. First results obtained by in operando study of such hydrogen electrode on the dry on palladium indicate that adsorbed CO_2 contamination might play a role in the pH buffering. This research on electrodes in the dry will also play a role in the GO part within the continuation of the excellence cluster RESOLV.

3. *Measurements of hydrogen distribution and effect on embrittlement*

The novel SKP and SKPFM based method for hydrogen mapping by making use of the hydrogen electrode in the dry has by now become an established tool for our research on hydrogen related topics, in close cooperation with other departments (see [151-156] and see p. 177).

Especially noteworthy is a fundamental research project where we try to evaluate the importance of the full 3D-parameter range of mechanical strain, hydrogen activity and exposure time on hydrogen induced material failure. We found that exposure time is an important factor, i.e. at a certain mechanical load and hydrogen activity, we observed that exposure time plays a role whether hydrogen induced degradation of the mechanical properties occurs or not. Since the experiments where performed with a ferritic model alloy, where the samples are quickly fully loaded by hydrogen, the effect of time is not simply due to

increase of the loading level. We found that under combined mechanical load and exposure to hydrogen activity vacancy formation occurs [151] that, most likely as hydrogen-vacancy pairs, leads to the observed failure. The formation of these vacancies is a slow process that leads to the observed time dependence. The microstructure, such as e.g. oxide inclusions play an important role here.

4. Semiconducting properties of surface oxide films

The semiconducting properties of surface oxides play a crucial role especially in atmospheric corrosion and coating delamination. One huge research field are zinc alloy coatings, where alloying with magnesium and aluminium can result to significantly enhanced performance [43-46]. Galvanic coupling between different phases can significantly modify the activity of the resulting surface oxides. Of special importance are the cathodic sites. We found that for Zn-Mg-Al alloys the finer the microstructure the smaller is the potential change upon changes between oxygen free and oxygen containing atmosphere. This is currently mainly investigated within the framework of an RFCS project (MicroCorr), where a combined SKP and SKPFM approach is applied. Of huge current interest is also the conductivity of the surface oxide of bipolar plates. In projects with industry as well as with the research centre Jülich we have started to investigate passivity and conductivity of different stainless steels in order to understand how to optimize their performance. One key technique we are establishing for that is current sensing AFM.

5. Intelligent self-healing concepts for corrosion protection

In the last years the main activities on self-healing have been 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 [65]. 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 [63,64]. Of special importance is the interfacial stability between conducting polymer and the metal surface [157,158]. A remaining challenge is 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. We found that embedding PANI capsules loaded with active agents into a matrix of conducting polymer (polypyrrole) is a promising way to achieve this. In principle we have shown in earlier works that continuous films of conducting polymer
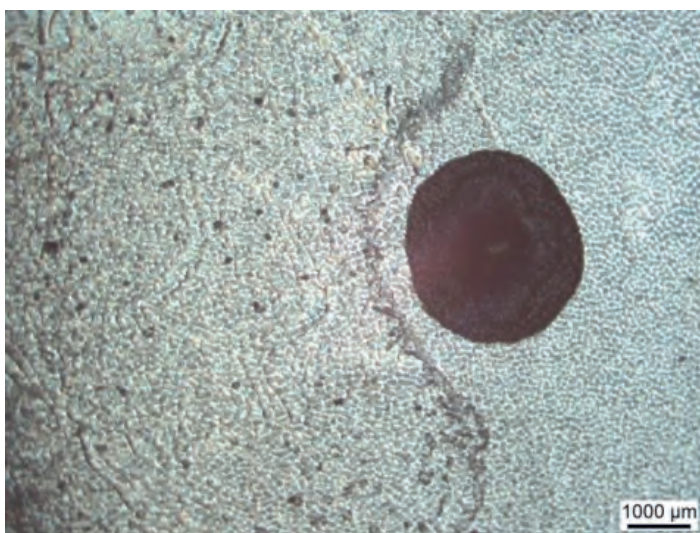
Fig. 4: *Photo of a partially delaminated clear coating on iron: around the black spot of PANI there is a clearly visible protection zone (delaminated area appears dark).*

must not be used for corrosion protection. Although they can provide excellent protection when there is no large defect, i.e. only small pinholes which can be easily passivated by the conducting polymer, they disastrously fail in presence of larger defects, by fast reduction and subsequent coating breakdown. Exactly this fast reduction can be made use of as fast spreading of a trigger for release. The self-healing induced by the released agents in turn stops corrosion and coating reduction and delamination, the reduced conducting coating being re-oxidised by atmospheric oxygen.

Discontinuous patterns of conducting polymers are also topic of research. Here we are interested in understanding the working mechanisms behind what we call protection zone surrounding deposits of conducting polymers (see Fig.4). These protection zones are several hundreds of micrometres wide. The corrosion driven delamination process stops for a certain time and then proceeds slowly until the protection zone is delaminated, too. The results of our investigations so far indicate that polarization of the interface by the conducting polymer and thus suppression of interfacial oxygen reduction is responsible for this. Anion migration from the conducting polymer vs cation migration from the defect seem to play a determining role in how well the protection zone occurs: the protection zone surrounding PEDOT (is reduced solely by simultaneous cation uptake) provides significant longer protection than the ones surrounding PANI or polypyrrole (reduced mainly by simultaneous anion release).

6. Novel developments with the Scanning Kelvin Probe

Based on our world leading expertise of the Kelvin Probe also novel application fields are explored. The recent development of spatially resolved high-sensitivity hydrogen detection by Kelvin probe

(see p. 45; p. 167) has sparked new research on the possibilities to further extent the applicability of the Kelvin probe. In cooperation with NORCE Norwegian Research Centre AS a novel Kelvin probe for outdoor use and for through metal corrosion is currently being developed.

Interaction Forces and Functional Materials (M. Valtiner)

The Interaction Forces group was active at the MPIE from 2012 until end of 2018. The group leader Dr. M. Valtiner left the institute in May 2016. After receiving an ERC grant at the MPIE in 2015 he was offered a W2 professorship at the University of Technology in Freiberg, Germany, and soon after he accepted a full professorship at the Vienna University of Technology in Vienna, Austria. He finalized the relocation of his entire group to Vienna in 2018. His newly established team there collaborates closely with our department in many research projects, including corrosion in confined spaces, ionic liquids at interfaces and hydration at interfaces (Resolv).

In the last six years, the research interest of the Interaction Forces group was focused on the broad areas of (1) adhesion of single molecules in wet environments, (2) molecular structuring at solid/liquid interfaces and (3) crevice corrosion at confined areas of Nickel and Nickel alloys in aqueous chloride containing salt solutions. The broader scientific aims of the group were (1) to gain insight into the molecular interactions at equilibrated and dynamically changing reactive interfaces, on (2) how molecular interactions translate into macroscopic interactions (scaling and proportionality laws), and on (3) developing new interferometry-based approaches to study dynamic corrosion processes *in situ* at crevice interfaces. A particular focus was also to establish how molecular structuring of solvents and ions at electrified interfaces influences the mentioned processes.

The major activities and achievements of the group can be summarized as follows in the different areas mentioned.

1. *Adhesion science and single molecule interactions at solid/liquid interfaces*

In a collaboration with M. Scott Shell (University of California at Santa Barbara, U.S.A.) approach to extrapolate macroscopic work of adhesion from single molecule Atomic Force Microscopy [52,54] was further expanded into studying hydrophobic interactions on a molecular scale, and comparing experimental results directly with molecular dynamic simulations [159]. This work was supported within the framework of the exceptionally competitive "Materials world network" grant scheme which is funding collaborative bilateral projects through the German Research Society (DFG) and the National Science Foundation (NSF) of the United States of America. In

the framework of this program, students and postdocs from the MPIE visited UCSB, and vice versa, for short (2 weeks) and extended (3 month) research stays multiple times between 2013 and 2016.

In addition, hydrophobic interactions between individual single molecules were tested [159] and hydrophobic interactions at extended scales were probed as a function of the ion concentration in solution [160] and as a function of the hydrophobic surface area [161].

Further, 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. Using bifunctional designer peptides it was possible to manipulate the number of interacting bonds in parallel and in series [162] and to modulate adhesion at will. Interaction free energies of peptides could successfully be measured with various surfaces [163,164]. Specifically, 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. Also the adhesion of sequences of the barnacle proteins [165] and functional groups that are abundant in mussel foot proteins [166], were successfully tested at the single molecular level.

2. *Molecular structuring at solid/liquid interfaces*

Electric double layers in static and dynamically changing systems were studied in a close collaboration with the cluster of excellence RESOLV at Ruhr-Universität Bochum. White light interferometry in an electrochemical surface forces apparatus allowed to simultaneous decipher both sides of an electrochemical solid/liquid interface [167], with microsecond resolution under dynamically evolving reactive conditions that are inherent to technological systems in operando. Quantitative *in situ* analysis of the potentiodynamic electrochemical oxidation/reduction of noble metal surfaces showed that Angstrom thick oxides formed on Au and Pt are metallic or highly defect-rich semiconductors, while Pd forms a non-metallic oxide. On the solution side, previously unknown strong electrochemical reaction forces were observed, which are due to temporary charge imbalance in the electric double layer caused by depletion/generation of charged species. The real-time capability of our setups 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 provides evidence that noble metal oxide reduction proceeds via a hydrogen adsorption and subsequent dissolution/re-deposition mechanism [167].

In collaboration with Frank Renner (University of Hasselt, Belgium) also battery fluids were intensively

studied [168]. Different wetting behaviour and wetting thicknesses of confined areas were observed, depending on the chemistry of the confining surfaces. This work suggests limits to effective wetting in battery devices and suggested that fluid transport along graphene pores is very effective compared to other materials. In a collaboration with the team of J. Maier (Max Planck Institute Stuttgart) glyme-based battery electrolytes were studied using the surface forces apparatus [169]. Based on comparing with interfacial spectroscopy data a model for the interfacial structure of triglyme electrolytes on muscovite mica was proposed. A surprising result of great fundamental significance is that the effective screening length measured by surface force apparatus at considerable lithium triflate concentrations (above 0.2 M) is substantially higher than expected from the Debye-Huckel theory, which is in line with data found for ionic liquids.

3. *Crevice corrosion, electrochemistry in confined spaces and high resolution imaging*

As already mentioned above the SFA was also utilized for corrosion studies in confined spaces [47, 170].

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Research Projects in Progress

Electrocatalysis (K. Mayrhofer)

Göhl, Mayrhofer, Ledendecker: Investigations of PtTM@HGS catalysts for fuel cell applications

Göhl, Mayrhofer, Ledendecker: Development of core-shell catalysts with improved durability

Kasian, Mayrhofer, Gault: Atomic-scale insights into surface species of electrocatalysts in three dimensions

Kasian, Mayrhofer: Fundamental investigation of stability of electrocatalysts for oxygen evolution reaction

Kulyk, Mayrhofer: Modelling of noble metal dissolution

Interface Spectroscopy (A. Erbe)

Chen, Kasian, Tecklenburg, Rabe, Mayrhofer, Erbe: Mechanistic investigations of electrochemical oxygen evolution on manganese-based model electrodes

Tecklenburg, Erbe: Defect formation in ZnO formed during corrosion processes

Pander, Tecklenburg, Wippermann, Erbe: *In situ* spectroscopic characterisation of the oxide-free silicon/electrolyte interface

Rabe, Erbe: Designing novel smart sensor interfaces based on a biologically abundant peptide motif: coiled-coils

Rechmann, Krzywiecki, Erbe: Synthetic molecular models for passive films

Ebbinghaus, Rabe, Erbe: *In situ* chemical imaging of processes during cathodic delamination

Corrosion (M. Rohwerder)

Beley, Palm, Rohwerder: Fundamental investigation of hydrogen in iron-aluminium intermetallics

Da Silva, Rohwerder: investigation of oxygen uptake and its effect on short term internal oxidation

Giesbrecht, Rohwerder: Fundamental investigation of the emersed electrochemical double layer

Kerger, Rohwerder: *In situ* investigation of electrochemical reduction and oxidation processes by ambient ESCA

Kim, Vogel, Rohwerder: Investigation of surface oxides on bipolar plates of stainless steels

Krieger, Springer, Zou, Rohwerder: Fundamental investigation of role of microstructure on hydrogen embrittlement and effect of exposure time

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

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

Tran, Groche, Rohwerder: Interface modification for optimized cold forging of aluminium-steel joints and their corrosion behaviour

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

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

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

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

Wu, Rohwerder: SKP for the investigation of hydrogen in metals: further developing the technique

Interaction Forces and Functional Materials (M. Valtiner)

Moreno-Ostertag, Spohr, Valtiner: Fundamentals of molecular adhesion under electrochemical conditions

Merola, Lorke, Valtiner: In operando study of corrosion in confined spaces using white light interferometry

Atomistic Modelling (S. Wippermann)

Adi Nugraha, Wippermann: Point defects at SiC/SiO$_2$ interfaces

Adi Nugraha, Wippermann: Anomalous temperature-dependent band gap shift of CdSe nanocrystals

Alaydrus, Wippermann: Multi-exciton generation in core/shell nanocrystals

Razzaq, Wippermann: Solitonic excitations in one-dimensional charge density waves with topological properties

Yang, Wippermann: Ab initio description of solid/liquid interfaces with finite electric fields

Khanifaev, Wippermann: Ab initio molecular dynamics simulations at constant electrode potential

Department of Microstructure Physics and Alloy Design

D. Raabe

Scientific Mission and Department Structure

We work on the relationships between **synthesis, processing, microstructure and properties** of compositionally and structurally **complex metallic alloys** including steels, magnesium, aluminium, superalloys, titanium and high entropy alloys. Focus is placed on **phase transformations,** design of **metastable phases**, **micromechanics** and complex **defect substructures** as well as their effects on the **mechanical** and **functional properties** [1-16].

We pursue these goals by developing and applying **advanced characterization** methods from the atomic level up to the macroscopic scale. Examples are chemically sensitive Field Ion Microscopy (FIM) which is based on the integration of atom probe tomography (APT), FIM and machine learning as well as correlative APT and scanning transmission electron microscopy (STEM) in concert with a reaction chamber and an ultrahigh vacuum (UHV)-cryo transfer unit [17-30]; Electron Channeling Contrast imaging under controlled diffraction conditions (ECCI) [31-35]; 3D electron backscatter diffraction (EBSD) and cross-correlation EBSD [36-38]; *in situ* micromechanical experiments correlated to local strain and hydrogen mapping [39-51]; and standardized bulk high-throughput metallurgy and mechanical testing [52-56]. Several of these techniques are developed and operated in collaboration with the MPIE-groups of G. Dehm, C. Scheu, M. Rohwerder and with R. Dunin-Borkowski (Ernst Ruska Centre in Jülich), J. Schneider (RWTH Aachen) and G. Eggeler (Ruhr-Universität Bochum).

We design **experiments based on theory-guidance** and conduct them under well controlled boundary conditions: For example for better understanding, quantifying and improving our atomic scale APT and FIM probing methods we collaborate with the department of J. Neugebauer on the simulation of field evaporation and image gas ionization as well as on the use of machine learning for crystallographic pattern recognition in APT data sets. Regarding **thermodynamics** and **structure–property relations,** we also collaborate with in-house *ab initio* experts for instance on phase equilibria for bulk and confined states and the thermodynamics of high entropy alloys [57-61]. Concerning **constitutive simulations** we have developed further our in-house modular **freeware simulation package DAMASK** (Düsseldorf Advanced Material Simulation Kit). This is a hierarchically structured model of material point behaviour for the solution of elastoplastic boundary value problems along with damage and thermal effects [40,41,62-70].

As an example, one topic where many of these fields of interest overlap in the department, is the interplay of **local chemical composition**, **phase metastability** and **transformations in confined regions**, i.e. at decorated lattice defects [1-12]. Correlative atomic-scale probing and thermodynamic theory show that in many alloys segregation to lattice imperfections is an ubiquitous phenomenon, yet, it is typically acquired through trapping of atoms to defects during tempering rather than being engineered

Fig. 1: *The Microstructure Physics and Alloy Design team.*

Research Approach	Fields of Interests	Method Development
Theory-driven **experiments**	**Segregation Engineering**: Structure and chemistry manipulation at defects	Düsseldorf Advanced Material Simulation Kit **DAMASK**
Devlopment of **advanced experimental** methods	Microstructure-sensitive analysis of **corrosion** and **hydrogen embrittlement**	**Correlative** Scanning Transmission Electron Microscopy and Atom Probe Tomography
Experiments under well **controlled boundary conditions**	Alloy design for **additive manufacturing**	**Combined** Field Ion Microscopy and Atom Probe Tomography
Quantitative comparison of experiment and simulation	**Metastable** phases and confined phase transformations	In-situ micromechanical experiments on **multiphase multicomponent alloys**
Materials and microstructures suited for **bulk processing**	Micromechanics of **high-mechanical contrast** materials	**Combinatorial** metallurgy
	Compositionally complex and high entropy alloys	**Quantitative** Electron Channeling Contrast Imaging
		3D Electron Back Scatter Diffraction

Fig. 2: *Research approach, interests and long-term method development in the Department of Microstructure Physics and Alloy Design.*

in a purposeful and property-directed manner. This has motivated us to conduct systematic **'Segregation Engineering'** experiments and develop from that corresponding alloy design and processing strategies where we utilize Gibbs and Fowler-Guggenheim – type decoration of lattice defects with the aim to turn these regions into chemo-structural entities that lead to beneficial mechanical and functional behaviour. This site specific manipulation of confined defect regions by chemistry has for example allowed us to tune lattice defects for improved local **cohesion**, **confined phase transformation**, **scattering**, **fracture toughness** and **impurity trapping**. Specific thermodynamic phenomena that we discovered in this context are composition-driven phase **transformations of dislocation cores** [1,5,9], confined **hydrides** [13,14], **stacking faults** [16,15], **spinodals** at grain boundaries and dislocations [1,5], and confined phase states and precursors phases preceding **nucleation** [1,5]. With these approaches and topics we conduct **materials engineering down to the atomic scale** (Fig. 2).

Research Groups

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

Research Groups

- **Mechanism-Based Alloy Design:** *D. Ponge*
- **Atom Probe Tomography:** *B. Gault*
- **Combinatorial Metallurgy & Processing:** *H. Springer*
- **Microscopy & Diffraction:** *S. Zaefferer*
- **Theory & Simulation:** *F. Roters*
- Alloys for Additive Manufacturing *(joint Max Planck - Fraunhofer group)*: *E. Jägle*
- Hydrogen in Energy Materials *(funded by ERC)*: *B. Gault*
- High Entropy Alloys *(funded by DFG)*: *Z. Li*
- Materials Science of Mechanical Contacts *(funded by BMBF)*: *M. Herbig*
- Advanced Functional Materials *(funded by BMBF, joint group with RWTH Aachen)*: *O. Cojocaru-Mirédin*

Fig. 3: *Research groups in the Department of Microstructure Physics and Alloy Design. The upper 5 groups (bold) are permanently funded. The bottom 5 groups are temporary initiatives, which are funded by grants.*

Mechanism-based Alloy Design (D. Ponge)

The group **'Mechanism-based Alloy Design'** works on the microstructure-oriented **design of advanced high strength steels**, **high entropy alloys** as well as on engineering **Al-, Ni- and Ti-alloys** [1-10,71-81]. Projects focus on multiple strain hardening mechanisms such as the interplay of dislocations, twins and deformation driven phase transformations. Of special interest are confined phase transformation phenomena at grain boundaries and dislocations. Projects in the group make intense use of the processing, mechanical testing and microstructure characterization facilities at the MPIE down to the atomic scale. Project are pursued in collaboration with partners from modelling, APT and microscopy. Theory-guided thermomechanical processing is a main pathway for optimizing the microstructures and mechanical properties of complex alloys. In this context a main objective of projects in this group lies in understanding and utilizing **elemental and mechanical partitioning** effects among neighbouring phases on the one hand and among the matrix and lattice defects on the other hand with the aim to adjust the (meta-)stability of local phase states. Depending on phase stability, deformation driven thermal transformations can be triggered such as spatially confined transformation-induced plasticity (**TRIP**) and transformation-inducted twinning (**TWIP**).

Main examples are the design of ultrafine grained, partially metastable, maraging, multiphase, medium-Manganese, martensite-to-austenite reversion and weight reduced steels for automotive, manufacturing and infrastructure applications.

Atom Probe Tomography (B. Gault)

The group 'Atom Probe Tomography (APT)' explores compositionally complex structural and functional materials based on the near-atomic scale information obtained from APT and FIM [13-30]. It operates three local electrode APT instruments (Cameca LEAP 3000X HR, LEAP 5000XS, LEAP 5000HR) and, for specimen preparation, three focused-ion beam microscopes, including one with a Xe-plasma source. A UHV-cryo transfer unit is used to transport sensitive materials between a glovebox with atmosphere control, and a reaction chamber. APT is a high-resolution characterization technique for 3D elemental mapping with near-atomic resolution. APT allows for studying nanoscale phenomena such as **precipitation**, solute **clustering**, **segregation** at defects, **complexions** and **partitioning** [1-11]. Important methodological progress lies in the use of correlative APT with scanning transmission electron microscopy and with FIM, as well as joint efforts with machine learning and *ab initio* simulations to aid the interpretation of the complex data. Projects are conducted in close collaboration with other groups and departments. On the metallurgical side, projects in this group are mainly concerned with Ni- and Co-based **superalloys, energy conversion materials, high- and medium Mn steels**, **stable hydrides**, in-**termetallic**s, **Ti**-alloys and **high entropy alloys** [1-30,83-97], often in close collaboration with the group **Mechanism-based Alloy Design**.

Combinatorial Metallurgy and Processing (H. Springer)

The group 'Combinatorial Metallurgy and Processing' 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 [52-56]. Innovative methods for the **accelerated synthesis**, processing and testing of bulk metallic structural materials are developed and applied, so that underlying metallurgical questions such as alloy- and processing-sensitive changes in strain hardening can be addressed more efficiently over a wide composition and processing range. The methods are thus referred to as '**Rapid Alloy Prototyping**' (RAP). This approach refers to semi-continuous high-throughput bulk casting, rolling,

heat treatment and sample preparation, and allows for evaluating base alloys in up to 50 different bulk conditions within a week. The approach is applied to metal matrix steel composites with high elastic stiffness, martensite-to-austenite reversion steels, weight reduced FeMnAlC steels, and medium and high entropy alloys.

Microscopy and Diffraction (S. Zaefferer)

The group '**Microscopy and Diffraction**' 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 [39]. 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. 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.

Theory and Simulation (F. Roters)

The group '**Theory and Simulation**' develops mechanism-based constitutive models [40,41,62-70] for a wide range of engineering alloy groups, focusing on crystal plasticity and multiphysics problems. Models range from phenomenological descriptions to physics-based formulations of **dislocation** slip, **twinning induced plasticity** (TWIP), **martensitic transformations** (TRIP), microstructural damage evolution and recrystallization effects as well as the associated temperature evolution. The 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. Owing to the crystalline anisotropy of metallic alloys, the constitutive laws assume a tensorial form both in their elastic and plastic formulations, i.e. they

T H E   D E P A R T M E N T S

129

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 in a fully coupled way using either the **Finite Element Method** (FEM) or a **Spectral Method** (FFT). The models are accessible through the modular simulation framework DAMASK with multiple academic and industrial users worldwide (https://damask.mpie.de) (see p. 50).

Alloys for Additive Manufacturing (E. A. Jägle)

The group '**Alloys for Additive Manufacturing**' was established in 2015 [82]. While particularly **Laser Additive Manufacturing** (LAM) is well-established to produce metallic parts, the design and further optimisation of alloy concepts tailored to match and utilize LAM requirements are still missing. Established alloys currently in use often do not exploit the opportunities inherent in this technique such as the rapid quenching, the intrinsic heat treatment coming from the next layers' deposition, and the metal-gas interaction during the process, leaving a gap for 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 operates an Aconity 3D SLM research size instrument and an in-house developed EIGA-type lab-scale atomizer for powder production. Projects examples are LAM of Fe-19Ni-xAl **maraging steels** with extremely high NiAl nanoprecipitation densities of 10^{25} NiAl precipitates per m^3, Al-Sc alloys and superalloys. Additional funding for the group comes from several projects of the German Research Foundation (DFG), including work on LAM of High Entropy Alloys.

Hydrogen in Energy Materials (B. Gault)

Recently a new group on '**Hydrogen in Energy Materials**' was established, funded by an **ERC Consolidator Grant** awarded to B. Gault. It is concerned with the **3D mapping of hydrogen** at near-atomic scale in metallic alloys with the aim to better understand hydrogen storage materials and hydrogen embrittlement. His approach is based on using an ultrahigh vacuum cryogenic transfer unit which connects two state-of-the-art atom probe microscopes with a scanning electron microscope fitted with a xenon-plasma gun. Through a precise control of H-loading into the specimen, the quality of the data will

be enhanced drastically while at the same time using data mining and machine learning techniques for data interpretation. More details on this new initiative are given on page (see p. 70).

High-Entropy Alloys (Z. Li)

The new group on '**High-Entropy Alloys**' which is funded by a grant of the German Research Foundation (DFG) explores novel high- and medium entropy alloys with respect to the identification of promising composition and process routes for new compositionally complex metallic alloys with excellent combinations of mechanical, physical and chemical properties based on the understanding of their structure-properties relations [91-104]. Conventional alloy design over the past centuries has been constrained by the concept of one or two prevalent base elements. As a breakthrough of this restriction, the concept of HEAs opens a new realm of numerous opportunities for investigations in the huge unexplored compositional space of **multi-component alloys**. While conventional alloys use strengthening mechanisms such as grain boundaries, **dual-phase** structure, dislocation interactions, precipitates and solid solution, our recently developed novel **interstitial TWIP-TRIP-HEAs** concept combines all available strengthening effects, namely, interstitial and substitutional solid solution, TWIP, TRIP, multiple phases, precipitates, dislocations, stacking faults and grain boundaries. This leads to the exceptional strength-ductility combination of the novel HEAs, exceeding that of most metallic materials. Several groups of HEAs with specific property spectra are currently studied by the group: These are alloys with excellent **strength-ductility** combinations; enhanced **resistance to hydrogen-embrittlement**; reduced mass density and high-strength; high-temperature refractory properties; and with multifunctional features such as good **cryogenic toughness** combined with specific **magnetic** features and **invar** properties (see p. 60).

Materials Science of Mechanical Contacts (M. Herbig)

The new '**Materials Science of Mechanical Contacts**' initiative is primarily funded by the federal ministry Bundesministerium für Bildung und Forschung. The group works on the metallurgical fundamentals of intense mechanical and environmental cyclic contact phenomena such as encountered in biomedical hip **implants**, **gears**, **bearings** and **railway** systems. In case of cyclic contact loading the microstructure never reaches a stable condition but evolves over time. Usually connecting liquid media such as lubricant or biofluids are involved leading to the formation of a reaction layer at the surface, the composition and structure of which can have an enormous influ-

ence on the overall lifetime of the part. The top layer of materials bearing such high cyclic contact loads for a longer time usually is comprised of a complex nanocrystalline multi-phase microstructure and thus understanding these phenomena requires joint crystallographic and chemical characterization from the micrometre down to the atomic scale. Details are given on p. 31.

Advanced Functional Materials (O. Cojocaru-Mirédin)

The group '**Advanced Functional Materials'** aims to understand the relationship between the chemical, electrical, and structural properties of microstructure-dominated functional materials such as solar cells and thermoelectrics. 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** and AgSbTe compounds for **thermoelectric applications**. To better understand these materials the group performs correlative studies using joint ECCI / EBSD / STEM, electron beam-induced current (**EBIC**) / **cathodoluminescence**, and **APT** [17]. The mission is to optimize the efficiency of solar cells and thermoelectrics based on the understanding of the interplay of local defect structures and 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 was originally financed by the NanoMat-Futur competition awarded by the federal ministry Bundesministerium für Bildung und Forschung. The group leader has a joint appointment as group leader both at RWTH Aachen and at the MPIE.

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: Structure and chemistry manipulation of lattice defects

Dislocations and **interfaces** influence mechanical, functional, and kinetic properties of alloys. They can be manipulated via **solute decoration** enabling changes in energy, mobility, structure, cohesion and promote local phase transformation. In our approach termed '**segregation engineering**' solute decoration is not regarded as an undesired phenomenon
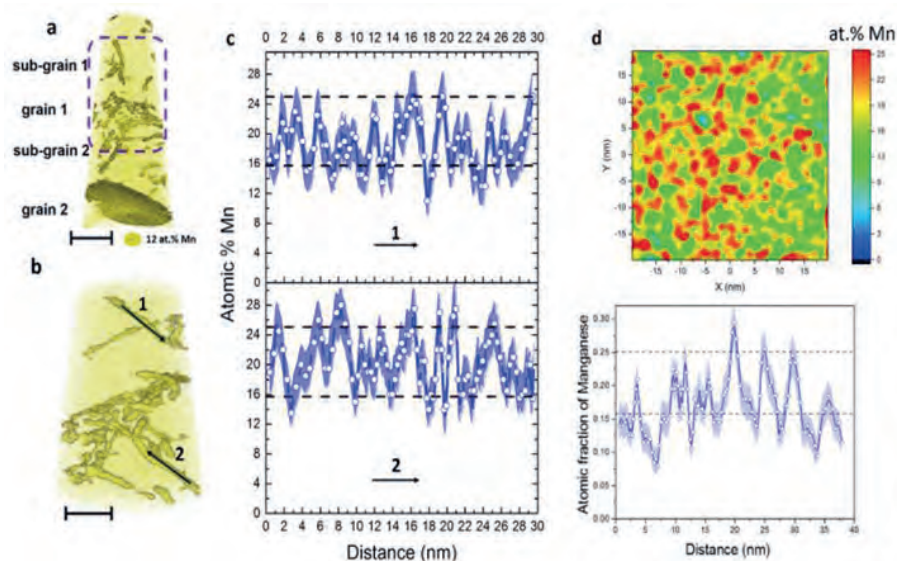
Fig. 4: *Locally confined spinodal decomposition states observed at lattice defects in a Fe-9 at. % Mn solid solution revealed by atom probe analysis. a) Dislocations decorated with Mn after 6h at 450 °C revealed by 12.5 at.% Mn iso-concentration surfaces to highlight the Mn-enriched regions showing a grain boundary and numerous dislocations decorated by Mn. Scale bar, 40 nm. b) Close-up on the middle section indicated by the dashed line showing decorated dislocations. Scale bar, 30 nm. c) 1D composition profiles along the two dislocations marked by the arrows in b). The points are the experimental values, which are connected by blue lines for better visualization. d) Spinodal decomposition viewed in the grain boundary plane and in form of a 1D profile through that plane [5].*
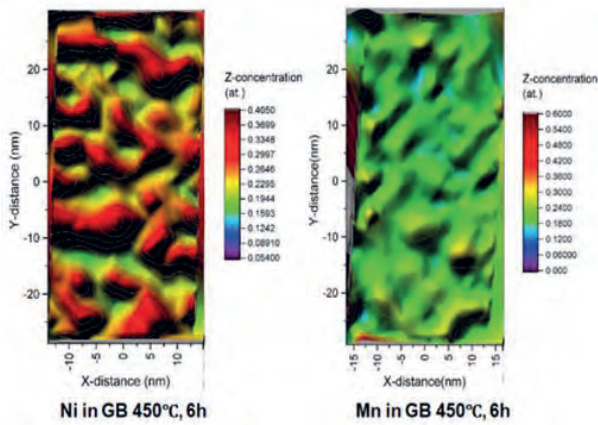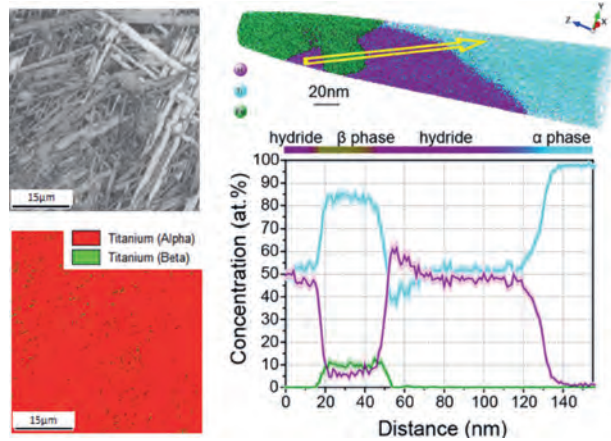
Fig. 5: *Spinodal decomposition viewed in the grain boundary plane in a FeMnCoNiCr Cantor High Entropy Alloy at 450°C after 6h acting as precursor state for intermetallic phase formation.*
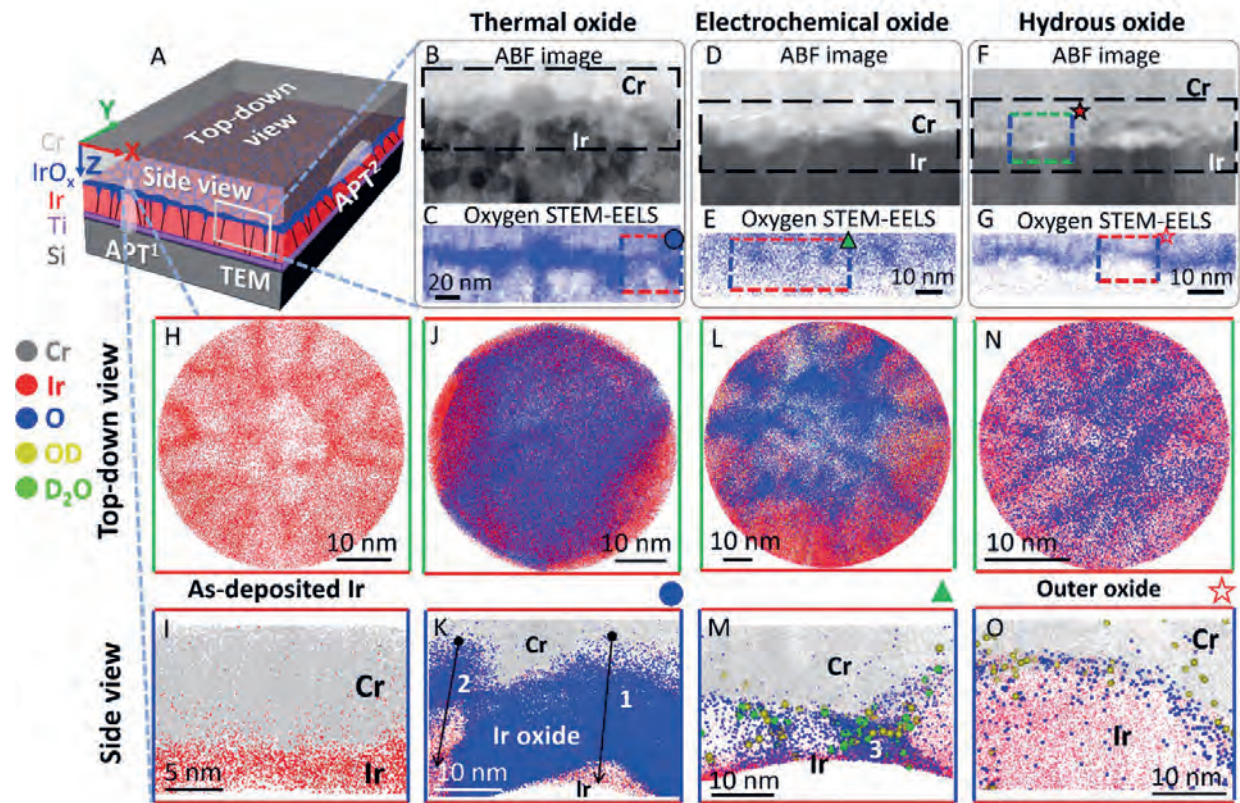

Fig. 6: *Multiscale characterization of solute H in a Ti-2wt%Fe matrix in the 950°C/45min-quenched state. Observation of hydrides on the α/β phase boundary.*

but it is instead utilized to manipulate specific defect structures and properties via composition change through Gibbsian decoration [1-10].

In that context we observed that **grain boundary (GB) segregation** and subsequent local austenite reversion of these decorated interface regions can turn interface embrittlement into toughness. 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 and fatigue resistance** [2]. Also, we discovered that Gibbs segregation to lattice defects, being a local equilibrium state, shifts the chemical working point from the material's bulk composition to a locally much higher composition. With this substantial shift in local equilibrium concentration at lattice defects compared to the bulk a number of thermodynamic phenomena can be observed at defects that do not occur in the adjacent bulk regions. Examples are spinodal decomposition, confined phase formation, complexion and confined phase transformation effects which are thermodynamically possible only at equilibrium doped lattice defects (see p. 169). Fig. 4 shows spinodal decomposition effects along dislocations and in grain boundary planes in the Fe-Mn system. The Fowler-Guggenheim segregation upon tempering shifts the decorated defects into a compositional range of the (local) phase diagram that is not readily accessible to the bulk. Similar interface **spinodal** decomposition effects were observed also on the grain boundaries of a FeMnCoNiCr Cantor high entropy alloy, where they act as precursor states for intermetallic phase formation (Fig. 5) (see p. 185).

Microstructure-sensitive analysis of corrosion and hydrogen embrittlement

One of the main challenges in the field of **corrosion science** lies in identifying the relations between **microstructure features** and the associated electrochemical or physical reactions, respectively, such as **oxidation** [28,29,97] and **hydrogen embrittlement** [30,47-51]. 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. In the context of imaging hydrogen and deuterium at the atomic scale particularly the new atom probe laboratory which is equipped with a cryo-transfer unit and a charging glove box is essential. Its use allows charged samples to be exchanged and probed among different microscopes and atom probes without any exposure to air or elevated temperatures (see p. 34) (Fig. 6). More details on the latest instrumental progress at the MPIE are presented on p. 70 and 179. Atom probe analysis plays also an increasingly important role in electrocatalysis, where it serves in revealing oxides and intermediate products of the first few atomic layers of thermally and electrochemically grown iridium oxides (Fig. 7) (see p. 163).

Alloy design for additive manufacturing

The **design of novel alloys** which are particularly suited to utilize the specific processing features associated with **Laser Additive Manufacturing (LAM)** is a key challenge in materials science. LAM processes allow production of small, custom-made parts directly from a Computer Aided Design model and metal powders. In the melt pool, the powder is completely melted. The resulting, dense

Fig. 7: *Multiscale characterization of the three-dimensional nanostructure of the first few atomic layers of thermally and electrochemically grown iridium oxides, efficient electrocatalysts for the oxygen evolution reaction. Atom probe analysis allows to image both the composition and its distribution of the metallic nanoparticles and also the oxides and some of the intermediate products which could be revealed by using heavy water, i.e. with deuterium [12]. This project is conducted in close collaboration with O. Kasian from the GO department, K. Mayrhofer from HGF Erlangen and T. Li from Ruhr-Universität Bochum.*

parts can have similar or even better mechanical properties than conventionally produced bulk metal. Two main aspects of the LAM process are particularly important in this context: Firstly, high cooling rates can be achieved during solidification (~10^2-10^5 Ks^{-1}) due to the small melt pool size and effective heat conduction into the underlying layers and the substrate. Secondly, as the laser passes by a previously deposited material volume during deposition of neighbouring tracks and subsequent layers, the material experiences cyclic reheating with gradually decaying temperature. This type of intrinsic heat treatment consists of sharp temperature pulses up to temperatures that may even be close to the melting point.

We work on several key material classes such as Ni-base **superalloys**, **tool steels** and **high strength Al-alloys** with the aim to design alloy variants which allow exploiting these processing features for manufacturing as-synthesized parts with improved properties.

One example is the successful combinatorial development of a model maraging steel consisting of Fe, Ni and Al, that shows a pronounced response to the intrinsic heat treatment imposed during the LAM process. Maraging steels belong to a class of

Advanced High Strength Steels (AHSS) that combine ultra-high strength with good toughness and ductility. They are of great importance in tooling, aerospace and energy industries. Without any further heat treatment, it was possible to produce a maraging steel that is intrinsically precipitation strengthened by an extremely high number density of 1.2×10^{25} m^{-3} NiAl nanoparticles of 24 nm size. The high number density is related to the low lattice mismatch between the martensitic matrix and the NiAl phase (Fig. 8).

Metastable phases and confined phase transformations

Utilizing the **segregation engineering** approach presented above we developed a class of novel materials which we refer to as **Reversion Alloys**. These are ductile intrinsically structured **micro- and nanolaminate alloys** that are formed in a self-organized way by reheating as-quenched microstructures and phases such as martensite in steels or Ti alloys so that spatially confined segregation-driven reversion from martensite back to the high temperature phase such as austenite in steels occurs at the lattice defects that were first decorated by **equilibrium segregation** (Fig. 9). This reversion heat treatment can be conducted at modest temperatures and times to create very fine regions of metastable phase revision
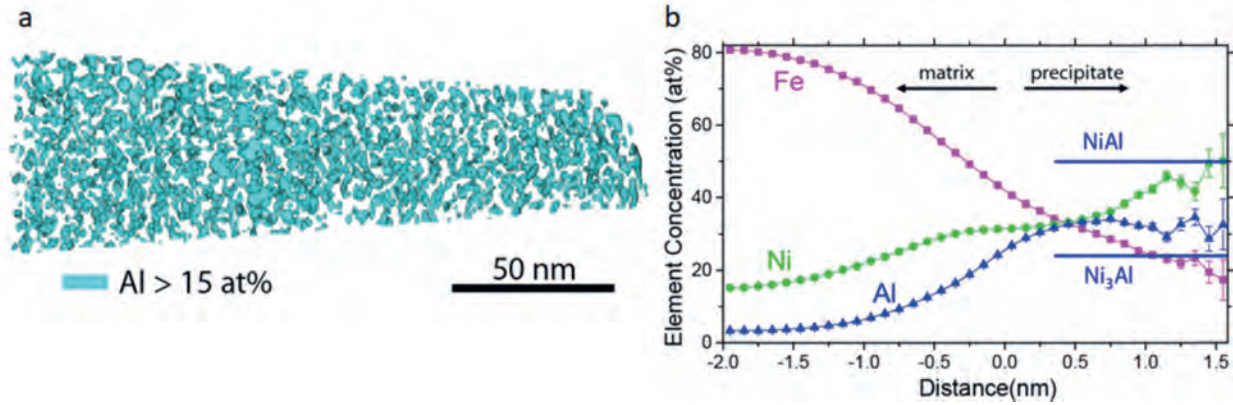
Fig. 8: *a) Precipitates in a lean Fe-Ni-Al LAM manufactured maraging steel visualized by drawing an isoconcentration surface at 15 at% Al. b) Corresponding proximity histogram plotting the chemical composition as a function of the distance to the isoconcentration surface. Expected Al concentrations for NiAl and Ni3Al are shown. The intrinsic heat treatment caused by the layer-by-layer build-up creates an extremely high number density of 1.2×10^{25} m^{-3} NiAl nanoparticles of 2.4 nm size and very high hardness. The work is conducted in collaboration with the Fraunhofer Institute for Laser Technology in Aachen.*
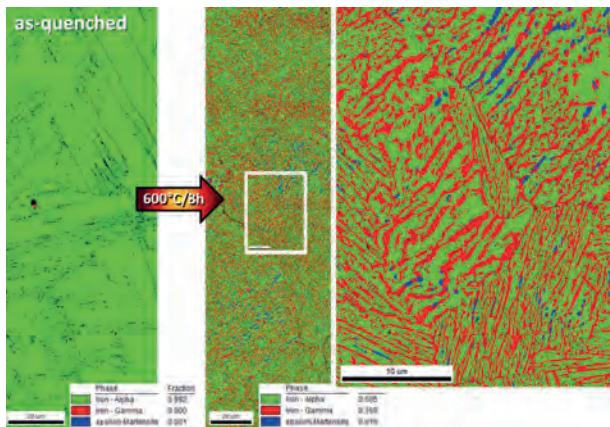
Fig. 9: *Grain boundary segregation followed by confined reversion transformation from as-quenched Fe-Mn martensite into metastable austenite enables the design of damask-type martensite-austenite nanolaminate steels where the solute decorated lath interfaces transform back to austenite.*

zones. This concept has proven particularly useful when designing nano-reversion steels with bone-like properties (Fig. 10). Such alloys unify **hierarchical nanostructures** consisting of a metastable nanol-aminated morphology. Upon local mechanical loading due to the propagation of a crack the metastable reversed austenite laminate layers undergo a TRIP effect and transform locally. Such local TRIP effect leads to crack blunting and additional strain hardening and thus to excellent fatigue properties.

Micromechanics of high-mechanical contrast materials

Multiphase microstructures containing phases with **high mechanical contrast** are the basis for many advanced alloys, particularly multiphase steels. As examples medium manganese-, quench-partitioning- and **dual-phase (DP) steels** take prominent positions in current efforts to quantitatively translate the
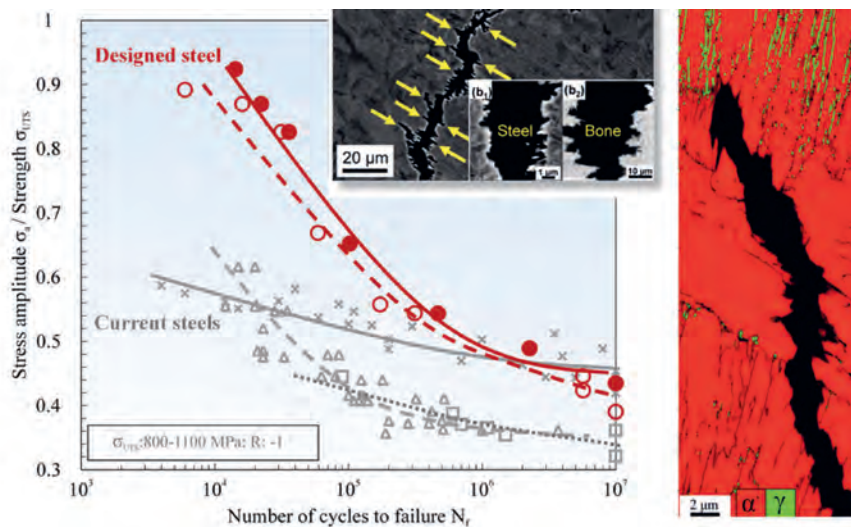
Fig. 10: *Microstructure and properties of a new nano-reversion steel with bone-like properties. The material unifies hierarchical nanostructures consisting of a metastable nanolaminated morphology. The EBSD map reveals that the metastable reversed austenite laminate layers undergo a TRIP effect and transform locally when exposed to the local stresses created by the crack. This effect leads to local crack blunting and additional strain hardening and thus to excellent fatigue properties [8]. The work was conducted in collaboration with C. Tasan from MIT and M. Koyama and K. Tsuzaki from Kyushu University.*
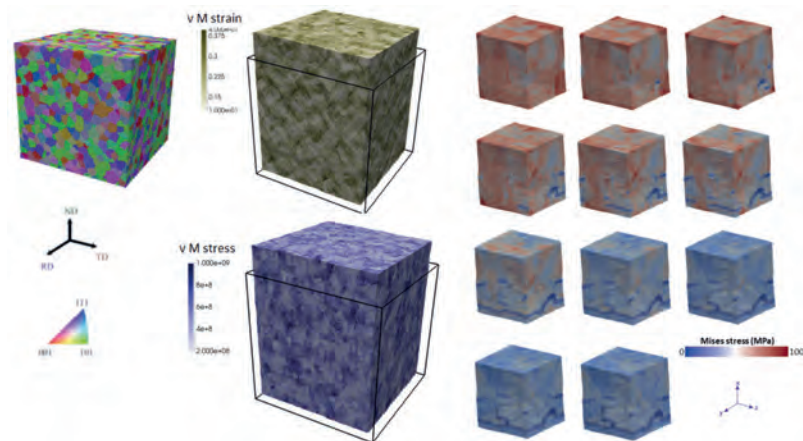
Fig. 11: *Representative volume element models of complex high-mechanical contrast microstructures such as encountered in multiphase steels or partially recrystallized materials (left). These simulations on artificial microstructural variants are used to systematically screen the influence of specific microstructural topologies, fractions as well as their strain hardening and damage parameters (middle). Particular efforts were recently placed on the development of advanced spectral solver methods for treating the associated boundary value problems more efficiently than the Finite Element method and on introducing damage models (right) into the simulations. All simulation tools are freely available under the umbrella of the DAMASK software package.*

features of complex microstructures into predictive models that can be used in processing and manufacturing. This is the core area of the micromechanical modelling activities in the department as described in more detail on page (see p. 50).

Handling the increased computational challenges associated with the underlying complex microstructures and the strong mechanical contrast among the phases requires not only improved **constitutive models** for strain hardening and damage but also an advanced numerical solution strategy that reaches beyond the established Finite Element solution approaches which are commonly used for solving corresponding **representative volume element models** [62-70]. These are simulations of artificial microstructural variants that are run routinely to systematically screen the influence of specific microstructural topologies, fractions as well as their strain hardening and damage parameters (Fig. 11).

To this end, efforts in the department were particularly devoted to develop and improve **advanced spectral method** based approaches for solving the associated boundary value problems and to replace the much slower de facto standard Finite Element owing to its numerical inefficiency and mesh-dependence.

Additional efforts were likewise devoted to develop coupled *in situ* experimental approaches that can be coupled with the micromechanical simulations in the philosophy of an integrated computational materials engineering (ICME) approach (Fig. 12). All modelling features described here are freely accessible in
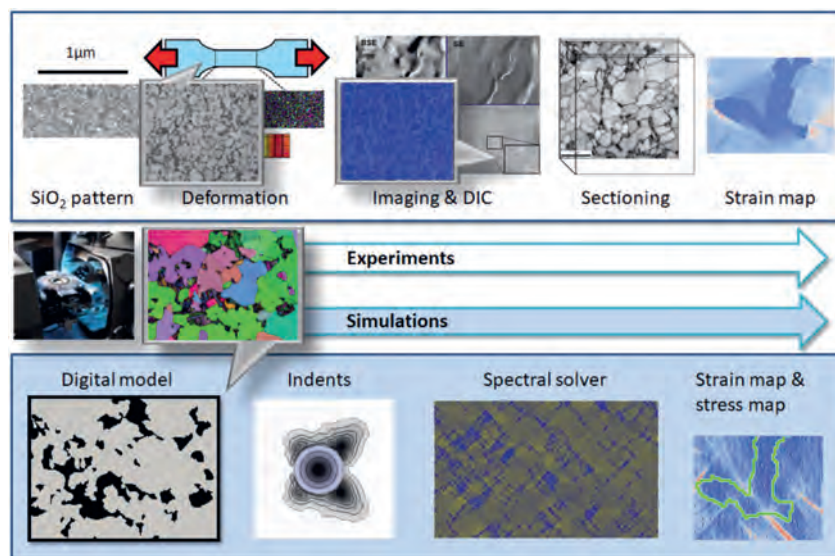
Fig. 12: *Example of an integrated computational materials engineering (ICME) approach applied to dual-phase (DP) steel: several types of in situ testing and parameter measurements are combined with micromechanical representative volume element models and full-field simulations using DAMASK.*
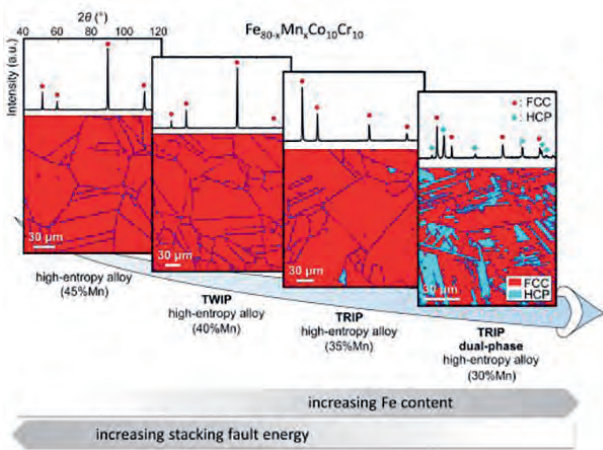
Fig. 13: *Change in the phase fractions (f.c.c.:red; h.c.p.: cyan) for the high entropy alloy system Fe(80-x)Mn(x) Co10Cr10 and the associated prevalent deformation mechanisms [94].*

our **Düsseldorf Advanced Materials Simulation Kit** (**DAMASK**) and can be downloaded at **https:// damask.mpie.de.**

Compositionally complex and high entropy alloys

Metallurgical alloying strategies have long been used to confer desirable properties on materials. Typically, it involves the addition of relatively small amounts of secondary elements to a primary element. A new alloying approach was recently introduced in which four, five, or more principal elements in high concentrations are combined to create novel materials called **high-entropy alloys** (HEAs). Some of these HEAs have already been shown to possess exceptional properties, exceeding those of conventional alloys (see p. 185).

Our specific approach to this field is a mechanism-based HEA design philosophy. This means that instead of conducting a systematic composition-screening of new HEAs we take a microstructurally- and **mechanistically-oriented design approach**. Traditional load carrying materials such as steels and aluminium alloys utilize specific strengthening mechanisms, considering also their dependence on temperature, stress and strain rate. Engineering such response over a more complex load path requires using not one effect alone but a sequence of mechanisms, including also their interplay and associated windows of operation. Examples are FeCrNi-based stainless or FeMnC-based TWIP steels, two alloy classes with some similarity to FCC HEAs [91-103]. These materials utilize marked **solid-solution** and **precipitation** strengthening, deformation **twinning**, ε-**martensite** and α-martensite, to name but a few characteristic mechanisms. The presence of solid solutions in these alloys not only strengthens the matrix but allows also for tuning of the stacking fault energy. Depending on its magnitude, its value affects the formation of partial dislocations and the occurrence of planar slip and double cross slip. This promotes the formation of rigid dislocation reaction products, dislocation storage rates, slip patterns and the evolving complex dislocation substructures. Reducing the stacking fault energy promotes the onset of twinning or martensite formation in the desired deformation, stress and strain rate window. The thermodynamic key-quantity for tuning all these features in these alloys is the **stacking fault energy** which can thus serve as one reliable governing alloy-design measure. In a mechanistic HEA design approach, the sequence of mechanism activation is also essential. For optimal strain hardening, dislocations alone are often not efficient since their multiplication can get
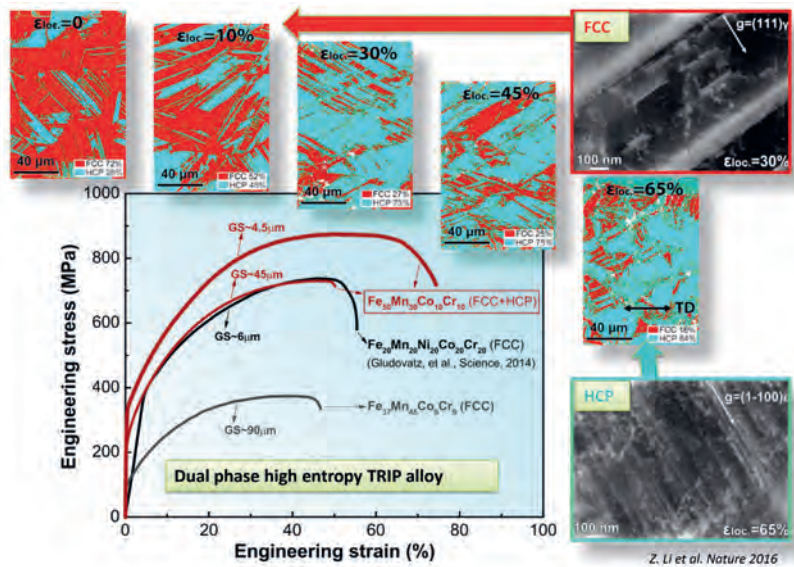
Fig. 14: *Engineering stress-strain curve, associated phase maps (red: f.c.c.; cyan: h.c.p.) and two exemplary dislocation substructures mapped by using Electron Channeling Contrast Imaging (ECCI) for the HEA Fe50Mn30Co10Cr10 (upper curve) for two different grain sizes (GS). The phase maps reveal the presence of the two phases prior to loading and the gradual martensitic transition from f.c.c. to h.c.p. at room temperature during tensile deformation. In the ECCIs, g is the diffraction vector [94].*

exhausted at early deformation stages, which is the result of the high initial strain hardening in common metals. Reducing the stacking fault energy enables mechanical twinning when the initial dislocation strain hardening gets weaker. When the additional strain hardening provided by mechanical **twinning** also gets exhausted, martensite formation could be activated if the stacking fault energy is sufficiently low (Fig. 13). We realize this alloy design strategy by developing for example non-equimolar and multi-phase derivatives of the Cantor alloy. Based on the equimolar Cantor alloy composition, several related variants with a smaller number of alloying components and non-equimolar compositions have been tested (Fig. 14).

Main Recent Breakthroughs

In several cases we achieved breakthroughs over the past years. Some resulted from **unexpected and unplanned discoveries** [1,5,6,16-18], others were harvested from **long term and systematic developments** [19,20,22,27,30,33].

Regarding method development we have made substantial progress in conducting site-specific sample extraction in conjunction with **correlated ECCI-EBSD-(S)TEM-APT characterization, correlative time-of-flight FIM experiments**, i.e. the operation of joint FIM and APT experiments **and UHV cryo-transfer among different probes** and **charging devices** of sensitive samples. These approaches enable profound insights into the interrelationships between structure and composition in complex micro-structures at atomic scale pertaining to the materials topics listed above.

Similar progress was enabled by rendering the **Electron Channelling Contrast Imaging** method quantitative by combining it with controlled diffraction conditions (cECCI). 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 modelling. 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 **https://damask.mpie.de**. It is used by a number of research groups worldwide. Regarding alloy design we have made substantial progress by introducing the concept of **non-equiatomic high entropy alloys in part with dual–phase microstructures** and the use of **interstitial alloying** in these materials.

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Research Projects in Progress

Kürnsteiner, Jägle, Raabe: New high strength aluminium alloys for additive manufacturing (industry, DFG)

Jägle: Precipitation kinetics during non-linear heat treatment in Laser Additive Manufacturing (DFG)

Springer, Tasan: Self-Healing Materials (DFG)

Gault: Topological Engineering of Ultra-Strong Glasses (DFG)

Roters, Yang, Diehl, Kasemer: Through-process simulation of microstructure, recrystallization, texture and mechanical properties (industry, DFG)

Zaefferer, Shanthraj, Herbig: Electroplastic mechanisms in Mg-, Al-Cu and metallic glass alloys (DFG)

Kamachali, Shanthraj, Diehl: Strong coupling of thermo-chemical and thermo-mechanical states in engineering alloys and processes (DFG)

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

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

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

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

Zaefferer, Raabe, Sandlöbes, Ponge: Synthesis, Characterization and local texture analysis and crystalline anisotropy in Mn-steels (DFG)

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

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

Li, Luo, Raabe: Hydrogen resistant high entropy alloys (AvH)

Sandlöbes, Friák, Raabe, Neugebauer: Fundamentals of the ductilization of Mg alloys

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

Tarzimoghadam, Gault, Ponge: Hydrogen embrittlement in metallic alloys (Industry, ERC)

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

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

Springer, Belde, Baron: Combinatorial synthesis, alloy design and phase boundary mechanics in stiffness enhanced multiphase steels (DFG)

Roters, Diehl: Constitutive and RVE simulation of the mechanical response of complex steels (Industry)

Li, Choi, Goto, Kirchheim, Dehm, Neugebauer, Raabe: Fundamentals of the strength of pearlite (Industry, AvH, DFG)

Gault, Koantis, Makineni, Povstugar, Choi, Raabe: Atom probe tomography of the chemical composition of interfaces in Ni-base superalloys (DFG, AvH)

Gault: Direct observation of atomic hydrogen (ERC)

Herbig: Intense mechanical frictional contact and white etching layers (BMBF)

Jägle, Zaefferer, Raabe: Microstructure and Processing of FeSi soft magnetic alloys (Industry)

Zaefferer: Microstructure and texture of Nickel alloys (Industry)

Department of Structure and Nano-/Micromechanics of Materials

G. Dehm

Scientific Mission and Concepts

The department was founded in October 2012 with a research focus on **microstructure physics and mechanical properties** of structural and functional materials covering especially **small length scales down to the atomic dimensions**. Our mission is to advance the understanding of deformation processes and constraining effects on mechanical and tribological material properties for both bulk and miniaturized materials by developing and applying quantitative tools, which are suited for small dimensions and high spatial resolution. The experiments are complemented by simulation techniques to understand their limitations and constraints and to aid data interpretation. Our research embraces the variety of microstructure elements from point defects, alloying additions, dislocations, interfaces to second phases and employs advanced structural characterization techniques to shed new light on the interplay of mechanical properties and microstructure evolution. This research interest includes initiation of plasticity, fatigue, fracture, slip transmission across grain boundaries, and phase transformations of grain boundaries to name the most prominent examples. In this context, scale bridging characterization techniques such as atomic resolved scanning and transmission electron microscopy (STEM/TEM), scanning electron microscopy (SEM), focused ion beam microscopy (FIB), X-ray diffraction (XRD) and advanced synchrotron methods are utilized and further improved by in-house development. **Our specialty is the integration of imaging and/or diffraction methods with external stimulus** of the sample **to identify the underlying mechanisms *in situ* while heating** [1-8], **straining** [9-16] **or electro-chemically altering the material** [17,18] and **to extract quantitative data**. Several instruments have been designed and built in-house making use of the expertise of the engineers and scientists in the SN department supported by the mechanical and electronic workshops of the MPIE.

The installation of this new department at the MPIE with its 5 research groups required substantial reconstruction work of hall 8-9, especially to host the microscopy infrastructure for the **Advanced Transmission Electron Microscopy** (**Dr. C. Liebscher, since April 2015)** and **Nano- and Micromechanics of Materials (Dr. C. Kirchlechner, since March 2013) research groups.** The reconstruction work started in December 2014 concluding a ~2 year planning phase and finalized in March 2018. 4 high-tech cubes were constructed with 2 of them fitted with active and passive electro-magnetic shielding to allow operation of the aberration corrected electron microscopy equipment at its resolution limits (see p. 37). Additionally, new TEM sample preparation laboratories were built. The department hosts now 2 atomic resolution TEM/STEM instruments, one probe corrected STEM/TEM (since 2015) with analytical tools (electron energy-loss spectroscopy and energy dispersive X-ray spectroscopy), one image corrected TEM/STEM (since end of 2017), and a field emission gun TEM/STEM (since 2006) equipped in 2018 with a fast CMOS camera allowing dynamic experiments to be recorded at ~200 frames per second. A new high resolution field emission SEM (since 2017) and a focused ion beam machine (since 2013) complement the microscopy facilities. The research group **Nanotribology (Dr. S. Brinckmann, since December 2014)** installed a nanoindentation platform with self-designed electro-chemical cells. The research group **Intermetallic Materials (Dr. M. Palm & Dr. F. Stein)** moved to the SN department in October 2012 from its interimistic home at the department of Microstructure Physics and Alloy Design (MA) and operates a modern thermodynamic laboratory (see p. 38). The research group **Synthesis of Thin Films and Nanostructured Materials (Dr. M. Ghidelli, since November 2018)** just recently commenced its work completing the originally proposed structure of the SN department. All 5 research groups strongly interact within and across the departments to contribute to the overall mission of the MPIE by developing new high-performance materials for use as high-tech structural and functional components. Additionally, the research groups also pursue their own scientific agenda to tackle central scientific questions within their research themes, which are discussed in detail later.

Despite the lengthy and difficult reconstruction work of hall 8-9 and the successful installation of the new facilities, several major achievements have been accomplished over the last years. Focusing only on the last 3 years, we advanced the understanding

of **dislocation - grain boundary interactions** by combining micromechanical testing of individual grain boundaries with *in situ* SEM and synchrotron based µLaue diffraction studies [9-11,19-23]. Interestingly, twin boundaries in Cu permit dislocation transmission of mirrored glide systems with a common Burgers vector at stresses as low as those required for cross-slip in a single crystal, in contrast to predictions by molecular dynamics [24,25]. The experimental results are further supported by strain rate sensitivity measurements of twinned bicrystals. They match with the corresponding single crystals, while in contrast for a randomly oriented penetrable Cu grain boundary the strain rate sensitivity becomes substantially higher. This can be explained by dislocation climb as the rate controlling step for the dislocation transmission process subsequent to dislocation absorption in the grain boundary and prior to emission from the grain boundary [9,10]. Other cornerstones of our micromechanical research are toughening mechanisms of materials and miniaturized **fracture toughness** measurements. We recently advanced our small scale fracture experiments to elasto-plastic fracture mechanics by monitoring the crack propagation via the sample stiffness evolution and *in situ* imaging techniques. In collaboration with the Max Planck Fellow Group on *Self Reporting Materials* headed by Prof. Jochen Schneider we applied these tools to resolve possible ductility in metallic glasses and layered crystals with high hardness, like Mo_2BC, which reveal moderate ductility in accordance with atomistic predictions [26-30]. Interestingly, even superlattice structures of hard and brittle materials can improve both, the hardness and the fracture toughness with reducing layer spacing [31].

Our recent atomic resolved STEM/TEM studies of **grain boundaries** revealed a **novel segregation phenomenon** at faceted grain boundaries in multicrystalline silicon [32], and for the first time experimental evidence of a chemically triggered **nano-faceting transition** in an Ag-Cu alloy [33,34]. Furthermore, two substantially different atomistic structures were detected indicating the **coexistence of two structurally different grain boundary phases** for a symmetric high angle tilt boundary in pure Cu. Such grain boundary phases are believed to have a large impact on material properties and are the central theme of the ERC Advanced Grant *GB CORRELATE*, which started in August 2018 to explore grain boundary phase transformations and their impact on material properties like grain boundary mobility and grain boundary mechanics (see p. 69). These research topics benefit from the strong in-house collaborations with the MA department providing unprecedented chemical sensitivity by correlated STEM/TEM and atom probe tomography (APT) as well as the department of Computational Materials Design (CM) with their *ab initio* tools predicting grain boundary structures and energies.

Materials development in SN revolves around **nanocrystalline alloys** and **intermetallic materials**. Severe plastic deformation, rapid quenching from the melt (including additive manufacturing), diffusion couples and physical vapour deposition are methods which we use to synthesize materials with exceptional strength and thermal stability - in some cases far from thermodynamic equilibrium. The materials portfolio ranges from alloys like Cu-Cr,Zr,Ta [3,4,35-38], high entropy alloys (or chemically complex alloys) [39,40], steels [2,41-43] to iron aluminides [44-58], Laves phases [59-62], and ferritic superalloys [63-67]. In several cases, close collaborations with industrial partners provide a stimulating exchange between basic research and application demands. Our observation that decomposition of cementite in a pearlitic steel by severe wire drawing leads to a tetragonal distorted C-rich ferrite which corresponds to a strain induced martensite initiated further studies on the fracture behaviour [68] and **microstructure evolution under tribological contact**. Our studies on surface wear of pearlitic steel using a sliding micro-asperity contact reveal plasticity in the cementite phase. It can be speculated that the plasticity within the Fe_3C lamellae of the pearlitic steel contributes to the decomposition process and C supersaturation of the Fe matrix.

The outcome of our research has led to several awards across all career stages; this includes a best poster award for young scientists at the Gordon Research Conference on Thin Films and Small Scale Mechanics (2016, N. Malyar), a best student talk award at the Nanobrücken conference (2017, W. Luo), a best paper award granted to F. Stein in 2016 by the International Commission of Alloy Phase Diagrams, the prestigious Heinz Maier Leibnitz award from the German Research Foundation (DFG) for early career researchers, which was granted to C. Kirchlechner in 2017 in "recognition of his outstanding achievements" [http://www.dfg.de/], and an ERC Advanced Grant in 2018 to G. Dehm - for which "the sole criterion for selection is scientific excellence" [https://erc.europa.eu/].

The recently founded SN department is already strongly connected within the MPIE, and with neighbouring universities and research institutes, like RWTH Aachen University, TU Dortmund, Research Center Jülich, and Ruhr Universität Bochum, where G. Dehm is appointed since 2012 as außerplanmäßiger Professor (adjunct Professor). The cooperations are well documented by joint publications, joint PhD students within the International Max Planck Research School SURMAT, and DFG funded research proposals like the Priority Programme (SPP 1594 Topological Engineering of Ultra-Strong Glasses, and SPP 2006 Compositionally Complex Alloys – High Entropy Alloys (CCA-HEA)) and Collaborative Research Centres / Transregio (TRR 188 Damage

Fig. 1: *2018 retreat at the Monastery Steinfeld.*

Controlled Forming Processes). The SN department hosts a Max Planck Partner Group in India on *Designing damage tolerant functional oxide nanostructures* (head: Ass. Prof. Dr. Nagamani Jaya Balila, Indian Institute of Technology Bombay) and the external research group *High Temperature Materials* headed by Prof. Gunther Eggeler, which continues the excellent interactions established during the preceding Max Planck Fellow group. Close research collaborations with France led to two DFG-ANR projects, one in the field of high entropy alloy thin film stability and fatigue, and the second focusing on the origin of fatigue damage in metals by developing and employing newest 3 dimensional µLaue techniques at the synchrotron facility ESRF in Grenoble. The large-scale collaborative EU research project HERCULES (http://www.hercules-2.com) develops within the FP7 long-term R&D Programme intermetallic materials for applications in large diesel ship engines with academic and industrial partners across Europe. The department hosts foreign guest researchers from abroad via the Erasmus programme, Alexander von Humboldt foundation, China Scholarship Council (CSC), Cambridge University summer student programme, and via secondments from institutes, universities, and industry.

Numerous conferences and workshops have been organized by members of the SN department. Recent examples are the 2018 Gordon Research Conference on Thin Films and Small Scale Mechanics (Lewiston, USA), the symposium Mechanical Properties and Adhesion at the International Conference on Metallurgical Coatings & Thin Films (ICMCTF) in 2017, 2018, and 2019 in San Diego, USA; the symposium Environmental, In-Situ and Time-Resolved Microscopy at the Microscopy Conference 2017, in Lausanne, Switzerland; symposia on Correlative Electron Microscopy & Atom Probe Tomography at the Materials Science and Engineering Congress - MSE 2018

in Darmstadt (C. Liebscher), on Experiments and Simulations towards understanding Tribology across Length-Scales at the MSE 2016 and at the MSE 2018 in Darmstadt (S. Brinckmann), on Mechanical Properties at Small Scales at the DPG meeting 2018 in Berlin, and on Experimental Nanomechanics at the 2018 European Mechanics of Material Conference in Nantes, France (C. Kirchlechner) as well as the biannual conference Intermetallics 2017 in Bad Staffelstein (M. Palm, F. Stein). In addition, several plenary, keynote and invited lectures were delivered at international conferences and institute colloquia by scientists from the SN department reflecting their high international visibility. A prestigious plenary talk at the European Mechanics of Materials Conference 2016, Brussels, Belgium; and keynote lectures at the Materials Science and Engineering Conference 2016 in Darmstadt and Israel Engineering Conference 2018 were delivered by G. Dehm, while invited talks were presented e.g. by C. Kirchlechner at the 2018 International Conference on Strength of Materials (ICSMA, Ohio, USA), C. Liebscher at Beijing University of Technology (2018), S. Brinckmann at the MRS 2017 Spring Meeting in Phoenix, M. Palm at the TMS 2017 Annual Meeting in San Diego, and F. Stein at the Thermodynamics of Alloys (TOFA) conference 2018 in Seoul. Our community services range from memberships in various selection committees (e.g. for the Allocation of Humboldt Research Fellowships, and for Independent Max-Planck-Research Groups), and in the Board of Governors of Acta Materialia Inc., to leading technical committees (DGM Fachausschuss Materialographie: C. Kirchlechner) and acting as editorial board members, reviewers and advisors for journals, funding agencies, and promotions of faculties.

Teaching and career development are two important areas promoted by SN members. This includes

involvement in summer and winter schools (2017 C. Kirchlechner organization of a summer school on Experimental Nano- and Micromechanics, G. Dehm teaching Stresses and Plasticity in Thin films at the GDRi Mecano General School 2018, M. Palm and F. Stein giving lectures at the MSIT Winter School on Materials Chemistry, 2018), teaching courses for the International Max-Planck Research School SUR-MAT and for PhD students at the MPIE, and regular courses at the Ruhr-Universität Bochum (G. Dehm, C. Liebscher, S. Brinckmann) and Montanuniversität Leoben (C. Kirchlechner). C. Kirchlechner received his habilitation in 2018 from the Montanuniversität Leoben. G. Dehm launched in 2015 career talks at the MPIE where companies present their activities in informal talks often followed by on-site visits. Not only steel companies, but also chemical, and electronic industry showed interest in this successful format which is organized by the PhD representatives of the MPIE under mentorship of G. Dehm (see p. 80).

Retreats of the SN department (Fig. 1) together with the independent research group *Nanoanalytics and Interfaces (NG)* (Prof. Christina Scheu) and external scientific guests are performed annually to discuss the individual research topics and to strengthen interactions within the department. The weekly seminar is intended to report on challenges and recent progress in the research topics of Master students, PhD students, postdocs, guest researcher and senior scientists.

The next chapter reports in more detail on the scientific achievements of the research groups of the SN department.

Scientific Groups

Nano- and Micromechanics of Materials (C. Kirchlechner)

The Nano- and Micromechanics Group: More than a mechanical microscope. Aim of the Nano- and Micromechanics group of the MPIE is to quantitatively understand, predict and alter fundamental mechanisms governing plasticity, fatigue and fracture of materials. For this purpose, we are isolating individual mechanisms – such as slip transfer of dislocations across a grain-boundary – by performing small scale mechanical experiments on samples with hitherto unreached small dimensions. But our work surpasses the local measurement of strength and toughness by far: A central aspect of our research is to link the mechanical behaviour to the underlying and evolving defect structures (e.g. dislocation types and densities, length and density of cracks and crack networks, etc.) which requires an advanced characterization toolbox with *in situ* capabilities.

After founding the group in 2013 we have successively developed our toolbox which today comprises *in situ* loading experiments simultaneously applying scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and synchrotron based X-ray Laue microdiffraction (μLaue) (see p. 41) while its three dimensional variant differential aperture X-ray microscopy (DAXM) is currently established. Today, this complementary toolbox permits to quantify topological changes of the sample during deformation, precisely measure the individual and collective density and type of dislocations, the local deviatoric strain tensor and track the grain-boundary character and orientations *in situ* under external stimulus.

A considerable part of our work focusses on the development of setups and analysis tools for extracting the relevant microstructural properties at the relevant length scale, which are often not available. One recent example is the development of DAXM with *in situ* capabilities, which is developed together with our partners at the ESRF in Grenoble, France (see p. 41). The tool allows for measuring the aforementioned microstructure parameters non-destructively with a voxel size clearly below 500 nm³ within unreached short experimental acquisition times. It is our vision to shed unprecedented light on the fundamentals of fatigue damage initiation and initiation of short fatigue cracks at grain- and phase boundaries in the upcoming years.

Our work is stimulated by key-questions concerning the mechanical properties of structural and functional materials. Structural materials of interest are various steels, high entropy alloys, intermetallics, and advanced magnesium alloys. In the field of functional materials we are focusing on conducting thin film materials and on advanced solder materials - often with a link to micro- and flexible electronics - and on tough hard coatings.

Single crystal plasticity. Our work on single crystalline materials was initially motivated by the "sample size effect", where the strength of single crystalline tremendously increases by reaching the micron and submicron scale. Recently, we have analysed the size scaling in tin at 0.6 of its melting temperature [69] and in copper at 400 °C [70], which is both of outmost importance for the reliability of advanced solder joints. Today we apply single crystalline micromechanics to understand the deformation behaviour of complex systems. For instance, together with the Intermetallics group we are currently exploring the deformation mechanisms in cobalt-based Laves phases where the role of off-stoichiometry on the mechanical behaviour is not understood – neither at room – nor at service temperatures.
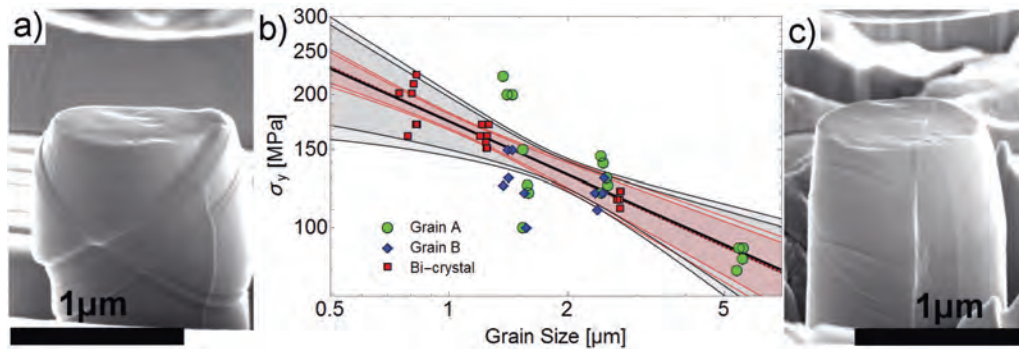
Fig. 2: *Micropillar compression on (a) single and (c) bi-crystalline pillars. (b) The yield stress of the bi-crystals is identical to the one of single crystals. The solid lines close to the straight fit following a Hall-Petch-like description indicate the 90, 95 and 99% confidence interval of the fit [72].*

A second set of projects on single crystals measures the anisotropy of the critical resolved shear stress (CRSS) in various materials. For instance, guided by the need of damage tolerant light-weight alloys, we are currently exploring the role of anisotropy of the CRSS on the formability of magnesium alloys. A second example is focused on the activation of anomalous slip in carbon containing ferrite in advanced dual phase steels, where we could show that the CRSS of {110} {112} and {123} slip is identical.

Finally, our group joined the worldwide efforts to understand the deformation behaviour of high entropy alloys (e.g. the Cantor alloy [40]), and, for the first time, reported on the micro-mechanical properties of hexagonal high entropy alloys [39]. In addition, together with the Advanced Transmission Electron Microscopy group we are currently exploring the role of atomic order, cross-slip and dislocation pile-ups on the critical resolved shear stress of the Cantor alloy.

Fundamentals of plasticity at grain- and phase boundaries. What stress is required to transmit a dislocation through a grain boundary? Is the transmission process strain-rate-dependent? What is the overall impact of dislocation slip-transfer to the strength of materials? Is there an impact of grain boundary structure and chemistry on the mechanical behaviour of bi-crystalline microsamples? These are the key questions motivating our grain boundary work with the ultimate goal to develop quantitative, mechanism-based material laws of dislocation slip transfer.

During the last 5 years we have extensively studied coherent Σ3 twin boundaries in copper. It was shown that the ideal slip transfer through such boundaries – which is possible only on 3 out of 12 slip systems – is similar to cross-slip. The slip transfer mechanism exhibits not only a similar activation volume [11], but also unexpected low transmission stresses of partly less than 20MPa further indicate the similarities of cross-slip and perfect dislocation slip-transfer [19]. Consequently, our early work was neither able to find dislocation pile-ups [15,16], nor revealed noticeable differences in the deformation behaviour of single

crystalline and bi-crystalline copper [71].

Our work on penetrable [20] and impenetrable [72] high angle copper grain boundaries shows that general slip transfer through non-Σ3 twin boundaries requires non-conservative motion of dislocations in the grain-boundary plane. As a consequence, the slip transfer itself is a highly strain rate dependent process. A fact which is not well-captured in today´s literature on dislocation slip transfer. As consequence, at small strain rates dislocations can frequently overcome grain-boundaries while slip transfer can entirely be suppressed at high strain rates. We were able to identify the strain rate sensitivity of a high angle grain boundary for the first time [9].

Finally, irrespective of the grain-boundary character, our investigated grain boundaries indicate that the strengthening effect at the micron scale is rather governed by the grain size than the grain boundary type (Fig. 2) [72]. One exception here is the above mentioned coherent twin boundary, which allows transmission in a cross-slip-like mode and, therefore, behaves similar as a single crystal.

Fracture at the micron scale. Fracture ultimately limits the lifetime of engineering components. But, what is the influence of the local microstructure on crack growth? Can we accurately determine the fracture toughness of phases, which cannot be synthesized in macroscopic dimensions? What is the fracture toughness of an interface? The Nano- and Micromechanics group performs research at the forefront of international efforts to extract meaningful fracture properties at the micrometre length scale.

A significant share of our work is devoted to assure reliable fracture properties at the micron scale. Linear elastic fracture mechanics (LEFM), well suited for brittle materials, are nowadays well established, also in small dimensions. Our group has assessed and quantified the role of testing setup and geometry on the extracted fracture properties in the past 5 years in collaboration with the Nanotribology group [73-
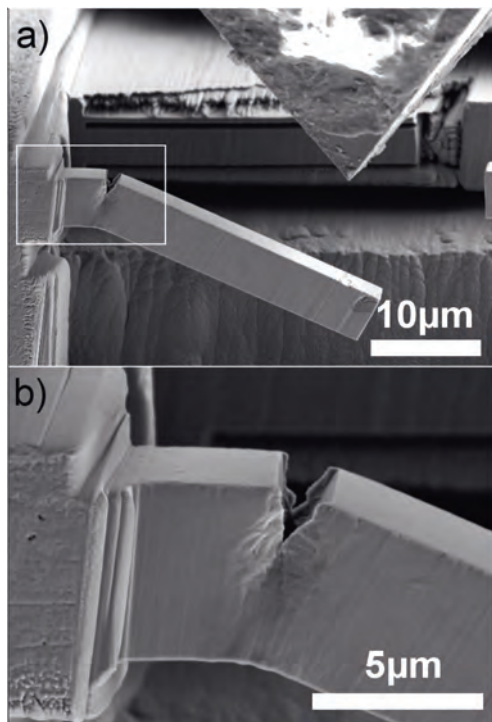
Fig. 3: *Microfracture experiment on a white etching layer (WEL). (a) The microbeam was bent by the diamond wedge visible at the top right. The zoom-in (b) shows the significant crack growth and ductile tearing of the nominally brittle WEL.*

75]. We further applied LEFM to identify toughening mechanisms based on super-lattice structures in hard coatings [31], to identify *ab initio*-based design criteria for damage tolerant metallic glasses [26,27] as well as hard coatings [28] and for identifying the Achilles´ heel of advanced solder materials [76,77].

Our current work heads towards reliable elasto-plastic fracture mechanics (EPFM) required to measure the fracture toughness of semi-brittle and ductile materials at the micrometre length scale. Essential ingredient to EPFM is the ability to track the crack tip *in situ*, for which we currently develop several different approaches based on the sample compliance as well as *in situ* imaging techniques. In parallel, we are applying this knowledge on the fracture toughness of white etching layers (see Fig. 3) in advanced railroad rails, on pearlitic steel wires with superior strength [68] and, together with the Nanotribology group on hydrogen embrittlement.

Switchable structural materials. Today's structural materials exhibit outstanding but predefined mechanical properties. To increase their adaptability e.g. for different crash scenarios in automotive applications we envision a new class of smart structural materials. Our key questions is if we can modify the strength of a material by an external stimulus in the required timescale of a few microseconds? While this question sounds like science fiction, it actually is currently brought into reality at the Micromechanics

group. The concept of this high-risk, high-gain project funded by the German VolkswagenStiftung is to modify the acting shear stress by so-called eigenstrain causing materials. First promising multi-physics finite element modelling identified advantageous material combinations which are synthesized as next step.

Advanced Transmission Electron Microscopy (C. Liebscher)

Group Mission. The Advanced Transmission Electron Microscopy (ATEM) group was established in 2015. The group develops, advances and employs methods in the transmission electron microscope (TEM) to unravel the fundamental atomistic aspects of complex materials and interfaces to establish a microstructure driven materials design. One of the key aspects is that **method development** is always targeted to solve a specific materials science related question [32,42,78]. For example, novel non-rigid image registration techniques are developed to enhance atomically resolved scanning TEM (STEM) towards fully quantitative imaging including atomic resolution strain mapping [42]. We are also **advancing** existing TEM and *in situ* TEM techniques [17] (seep. 40) to extend their limits and with this enable novel insights into the atomic structure of complex materials [38,78-82] and material defects [32,33,83]. The atomic scale correlation of aberration corrected STEM and atom probe tomography (APT) [32,42,78] is an example where we could uniquely establish the connection of the atomic structure of grain boundaries in Si and their solute segregation behaviour [32]. Furthermore, the advanced TEM methods are **employed** to design nanostructured materials based on their atomistic structure [35,42,81,84,85]. This culminates in the evolution of novel multicomponent materials with tailored nano-precipitates for advanced applications [86].

Facilities. The group utilizes four TEMs. The CM20 (Thermo Fisher Scientific) with LaB_6 emitter is used for conventional diffraction contrast imaging and electron diffraction experiments and serves as a training platform for TEM beginners. The JEM2200FS (JEOL) is equipped with a Schottky field emitter, an in-column omega energy-filter and an energy dispersive X-ray detector. The JEM2200FS is the main platform for *in situ* TEM experiments and was upgraded with a high-speed CMOS camera (TVIPS GmbH) in January 2018. This will also enable us to further advance *in situ* liquid cell experiments in collaboration with the department of Interface Chemistry and Surface Engineering (GO) and the Poseidon liquid cell holder (Protochips) [17]. Since April 2015, the probe-corrected Titan Themis 60-300 (Thermo Fisher Scientific) is one of the major microscopes for atomic structure observations and
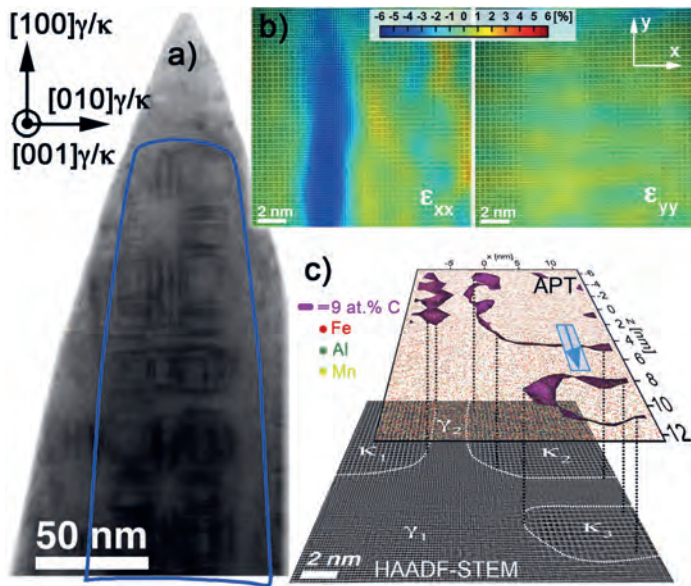
Fig. 4: *a) Overview annular bright field (ABF) STEM image of a needle shaped specimen. The volume of the APT reconstruction is outlined in blue. b) Atomic resolution strain maps obtained in the apex of the APT specimen. c) Direct correlation of STEM and APT resolving both the atomic lattice structure and composition [42].*

atomic scale analytics. The microscope was installed in an intermediate room in 2015 and moved to the microscopy laboratories by the end of 2017, where it was finally commissioned in April 2018. The last instrument completing the advanced TEM facilities is an image corrected Titan Themis 80-300 (Thermo Fisher Scientific). The instrument was commissioned in October 2017 (see p.37).

Mechano-chemical coupling at coherent interfaces. The aim of this research project was to extend the current limits of correlating TEM with APT by using aberration corrected STEM methods to unravel the intimate relation between the local strain state and composition at coherent interfaces [42]. An effective way of strengthening a solid solution is obtained by the dispersion of coherent, nanometre-sized precipitates. In low-density steels with high manganese (Mn) content, κ-carbide nano-precipitates, with a size in the range of 20 nm to 50 nm, are the major strengthening phases. These ordered Fe_3AlC type precipitates exhibit a slightly larger lattice parameter than the face centred cubic (fcc) Fe matrix and hence complex internal strain states evolve. We developed a methodology to quantify local lattice strains by atomic resolution STEM in a needle-shaped specimen, as shown in Fig. 4a and b. The elemental distribution and composition in close proximity to the interfaces can then be probed with unprecedented elemental sensitivity in the same sample by APT illustrated in Fig. 4c. Atomic resolution strain mapping reveals that the lattice of 2-3 nm nanometre wide fcc-Fe matrix channels is tetragonally strained to compensate for the lattice mismatch. Atomistic simulation establishes that such a tetragonal lattice distortion has a strong

effect on the C solubility and with this affects the growth kinetics of the precipitates as well as the interaction with dislocations during deformation.

Unexpected segregation behaviour at faceted grain boundaries. A major interest of the ATEM group is to unravel transitions and transformations at grain boundaries [32,33,83]. These planar defects are fundamentally determining the properties of advanced materials and the influence of grain boundary transitions on their properties is rarely explored. The aim of our work is to establish a generalized understanding of interfacial transitions across different types of grain boundaries and material systems. We are currently contrasting interfacial transitions in face centred cubic (fcc) Cu with controlled additions of Ag and S [33,83] with that in body centred cubic (bcc) Fe(Al) and Fe(Si) alloys. The atomic scale experimental observations are complemented by atomistic simulations in collaboration with Dr. Timofey Frolov (Lawrence Livermore National Laboratory, USA) and the CM department of the MPIE. In a more specific research highlight, we employed the previously described methodology correlating STEM with APT to discover the segregation of impurity elements C and Fe at nano-faceted grain boundaries in multicrystalline Si [32]. The majority of grain boundaries in this wafer material are large angle grain boundaries that often dissociate into nanoscale facets, whenever the overall grain boundary inclination deviates from
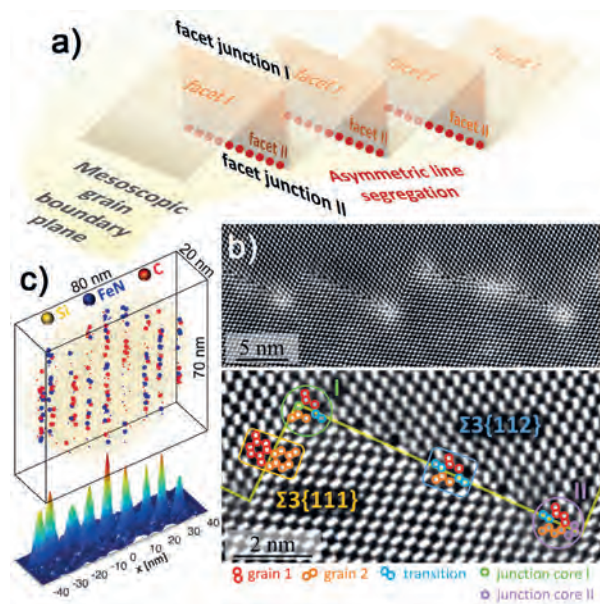
Fig. 5: *a) Schematic illustration of grain boundary faceting and its influence on solute segregation. b) Strain sensitive STEM images of a faceted Σ3 grain boundary and junction core structures. c) Corresponding APT reconstruction at the grain boundary highlighting the line segregation of Fe and C [32].*

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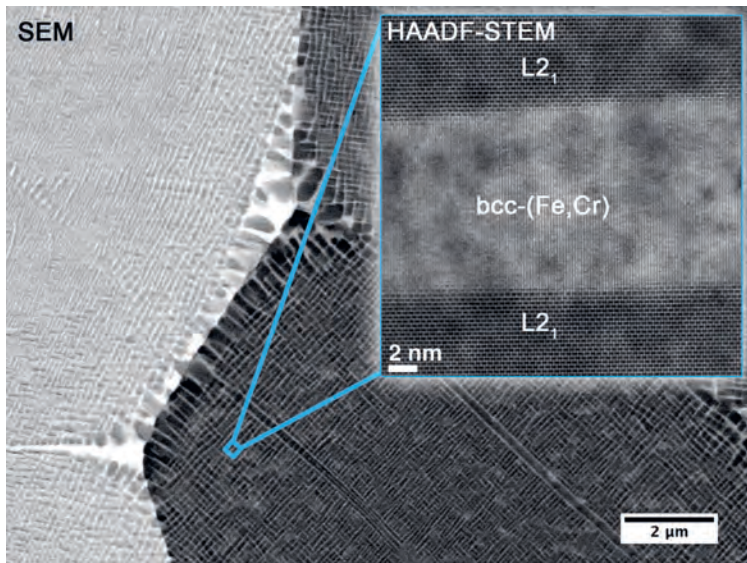
Fig. 6: *SEM and HAADF-STEM images of an $Al_{25}Cr_{15}Fe_{30}Ni_{20}Ti_{10}$ (at.%) compositionally complex alloy.*

the symmetric orientation. Hence, the grain boundary is composed of planar grain boundary facets that are separated by two different types of linear grain boundary facet junctions, as shown schematically in Fig. 5a. Atomic resolution STEM imaging shown in Fig. 5b reveals that the local atomic reconstruction in both facet junctions differs substantially and with this an asymmetric strain state develops. The low impurity concentrations in the lower ppm range require correlated APT measurements to uniquely locate the impurity atoms at these topologically complex interfaces. In contrast to the often assumed planar segregation, the impurity elements are forming segregation lines only within one particular type of facet junction, as seen in the APT reconstruction of Fig. 5c. With the aid of atomistic simulations performed by Dr. Liverios Lymperakis (CM), we were able to connect this unexpected segregation behaviour to the local strain state at the facet junctions. Both, the finite size of the grain boundary facets and the junction core structures leads to the evolution of an asymmetric strain state and segregation is favoured in facet junctions with largest compressive strains.

Development of nanostructured compositionally complex alloys. The method development and advancement of characterization techniques is utilized to design and understand the microstructure-property relationships in novel compositionally complex (CCA) [86] and high entropy alloys (HEA). In this alloy concept, an equal amount of at least five alloying elements is added to establish highly supersaturated solid solutions (HEA) or novel precipitate structures (CCA) that are otherwise not attainable with classical alloy design concepts. The compositional complexity strongly impacts the properties of these materials and by combining advanced TEM characterization with *in situ* TEM deformation, we are shedding new light on the atomic scale deformation behaviour in the Can-

tor alloy. We are particularly interested in resolving the effect of short-range order on the dislocation mobility, which is of utmost importance to decode the unique properties of HEA. Furthermore, two projects are focusing on the design of novel CCAs funded within the DFG priority programme 2006 Compositionally Complex Alloys - High Entropy Alloys (CCA - HEA). The first project is concerned with the development of precipitation hardened CCAs through selective laser melting of HEA powder samples. This work is in collaboration with Dr. Uhlenwinkel (University of Bremen) and Dr. Eric Jägle (MA), where, in a first step, we are focusing on the atomic scale characterization of phase separation processes in bcc-type CCA powders with an interconnected, nanoscale *B*2 network. The second project started in November 2017 and is a collaborative effort together with the department of Materials Chemistry at RWTH Aachen University. We are aiming to design novel alloys with tailored precipitate structures for advanced high temperature applications. The composition space investigated in the ATEM group is centred around the equimolar $Al_{20}Cr_{20}Fe_{20}Ni_{20}Ti_{20}$ (at.%) alloy. The goal is to establish materials that are comprised of abundant materials with low density and exhibit excellent mechanical properties up to temperatures of 900°C. To achieve this, we allow the composition to be relaxed from the equimolar one, opening up an enormous phase space that is explored by combinatorial synthesis techniques coupled with advanced material characterization. A key point of the project is to design materials by optimizing their nano- and microstructure. Representative secondary electron microscopy (SEM) and high angle annular dark field (HAADF) STEM images of a promising alloy candidate with composition $Al_{25}Cr_{15}Fe_{30}Ni_{20}Ti_{10}$ (at.%) are illustrated in Fig. 6. The microstructure is composed of a high density of fully coherent $L2_1$-type precipitates embedded in a highly supersaturated body centred cubic (bcc) solid solution matrix of nearly 50 at.% Fe and 50 at.% Cr.

Nanotribology (S. Brinckmann)

Group mission. The research group was established in December 2014 and focuses on the investigation of microstructure evolution during friction and wear. The projects study tribology using micrometre asperities that mimic single asperities of macroscale components, thereby aiming to understand fundamentally the irreversible mechanisms that result in energy and structural loss. The investigated evolution processes include grain refinement, plasticity,

phase formation and dissolution. Although we focus on the dry contact of metals with hard asperities, some projects probe the metal on metal contact in the presence and absence of lubricants.

Additionally, we use continuum simulations to further the insight into microscale fracture and toughness of brittle and ductile metals in collaboration with the Nano- and Micromechanics of Materials group. Moreover, we carry out experiments on hydrogen embrittlement of metals by developing procedures to quantify dislocation plasticity in the presence of hydrogen and evaluate the nucleation strength of dislocations.

Tribology of steels. Multiple parameters affect tribology: material properties of both materials in frictional contact, surface roughness, normal force, relative velocity, lubricant, temperature and duration of tribological loading. The influence of the parameters and their interaction are generally nearly impossible to decipher. It is our approach to decrease radically the number of parameters to simplify the tribological interaction with the aim to understand and analyse individual mechanisms. Therefore, we study the contact with a non-deforming (infinitely stiff and inert) diamond micrometre asperity. The room-temperature dry single stroke experiments use a low velocity, which does not heat the material. Therefore, only the normal force, contact radius and relative velocity are parameters in our experiments. The studies on an austenitic stainless steel (see Fig. 7c) [87,88] introduced the separation into elastic (that follows an adopted Hertzian model) and plastic deformation (that can be determined from the metal hardness). Moreover, that study showed asymmetric slip-pattern formation on the metal surface although the tribological loading is symmetric. The project revealed that the crystal orientation and the free-surface proximity introduce an asymmetry that result in the particular slip pattern. A study on Cu revealed that the slip steps in the wear track result also in the formation of surface cracks, which depend on the crystal orientation only. A DFG funded project (BR 3947/5) started in 2018 to investigate the crack formation in fcc and bcc steels during tribology.

In addition to the investigation of monolithic materials, we evaluate the microstructure evolution of pearlitic steel (see Fig. 7a), which consists of 200 nm thick cementite (Fe_3C) lamellae and a ductile ferrite matrix [89]. The project showed that the lamellae are bending plastically with strains up to 40% (Fig. 7b), which is atypical for Fe_3C. We found also that the bending strains depend on the distance from the wear track. Micromechanical specimens of Fe_3C were used to quantify the fracture toughness and yield-strength. It was shown that Fe_3C can deform by plastic slip at the microscale.
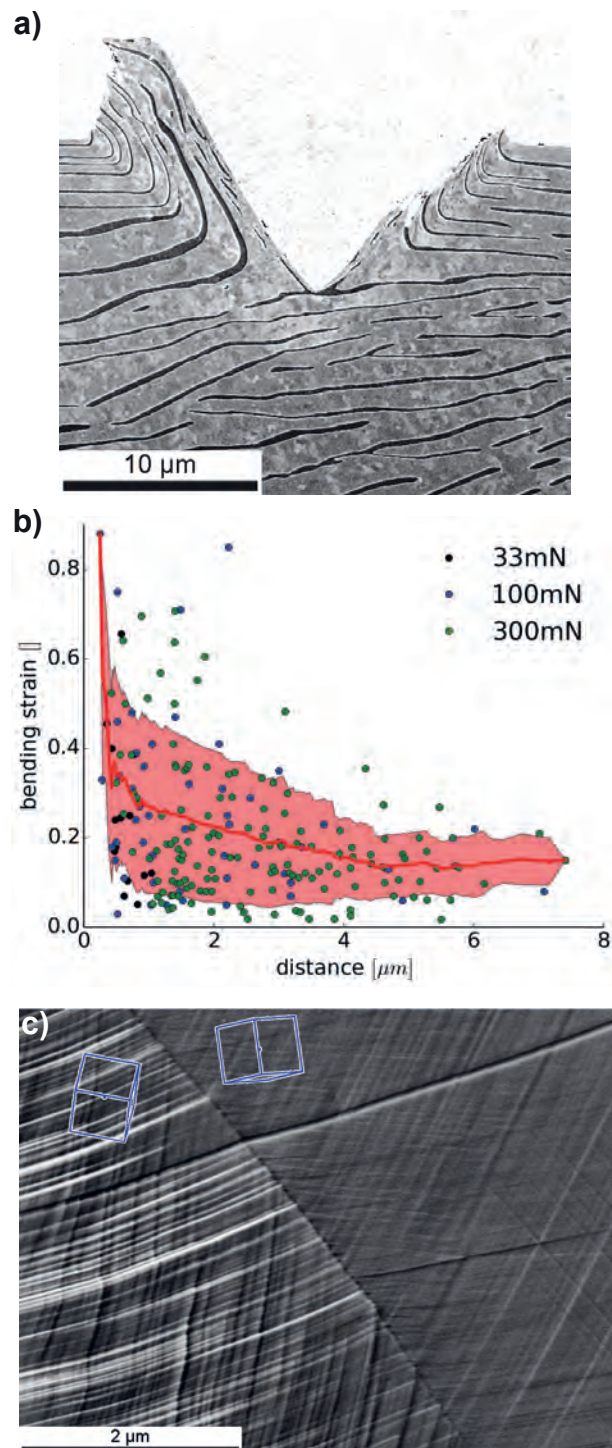
Fig. 7: *(a) Wear track in pearlitic steel, the cementite lamellae are plastically deforming. (b) Bending strains as a function of the distance from the wear track for different normal forces. (c) Tribology induced slip steps intersecting a grain boundary in an austenitic stainless steel.*

Mechanochemistry of tribological surface layers. Lubrication additives result in surface layers and in improved wear and friction properties. However, a number of parameters influence the surface layer formation and disagreement exists in the scientific literature on the influence of the parameters. In collaboration with the RWTH Aachen University, we

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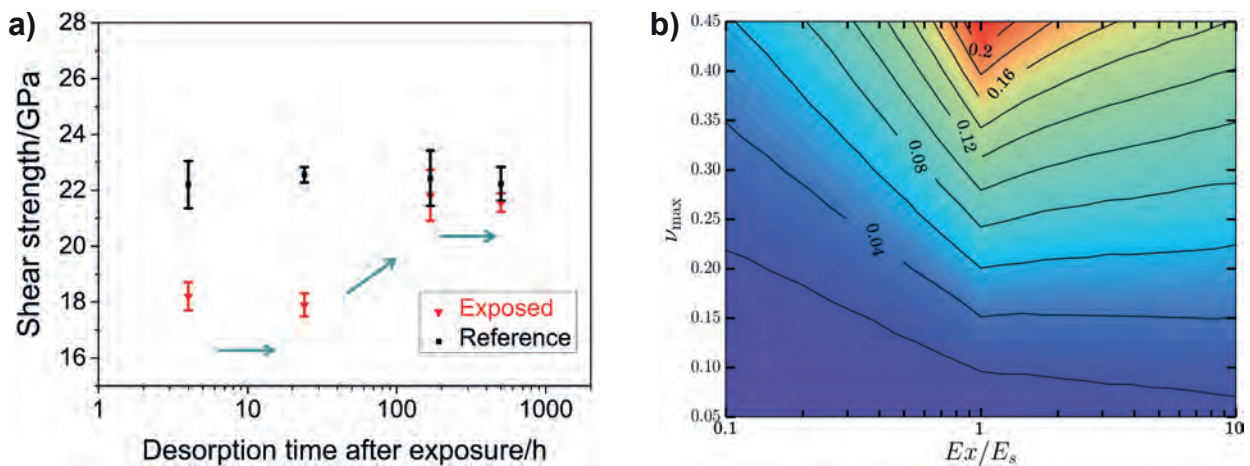
Fig. 8: *(a) Shear strength of tungsten as a function of the desorption of hydrogen, i.e. time after H exposure. The shear strength of dislocation nucleation was determined by nanoindentation. (b) 3D Fracture toughness evaluation for an anisotropic material (with a ratio of Elastic moduli in the axial and perpendicular direction E_x/E_s) and for different Poisson ratios: the fracture toughness is up to 20% larger in the centre of the crack path than at the surface.*

developed a novel experimental method that uses cyclic compression on the micro- and macroscale and that focuses on the mechanical properties in tribology. Following the steel on steel experiments with lubricant on the microscale, a number of characterization techniques identified a P, S and Zn rich layer of 100 nm thickness, which is similar to conventional tribolayers. Hence, the novel method is able to further the understanding of tribological surface layers [90].

Hydrogen embrittlement of metals. Hydrogen embrittlement of metals is of general importance in engineering applications. In tribology, it is of specific significance since hydrogen is linked to the growth of white-etching-areas, which result in catastrophic failure. This research group investigates the hydrogen-metal interaction using simplified loading conditions.

We perform nanomechanical testing while charging *in situ* the samples with hydrogen (see p. 42). The techniques use nanoindentation, nanoscratching, micropillar compression and microcantilever bending to study independently grain interiors, grain boundaries or precipitates. Two setups were designed in-house to charge electrochemically a sample and these setups were incorporated to the G200 nanoindenter for *in situ* testing [91]. In the "front-side" charging cell, the electrolyte is in contact with the sample surface allowing fast charging, while a "back-side" charging setup preserves the intact sample surface for additional post-deformation characterization. One example is the study of dislocation nucleation and hydrogen mediated plasticity in ferritic FeCr alloys, in which we found a decrease of the shear strength and an increased hardness as function of the hydrogen content. This work is funded by the DFG (DU 1628/1) since 2016.

In collaboration with the Forschungszentrum Jülich, we investigate the hydrogen-tungsten interaction using micromechanical experiments. After charging the metal with deuterium, we execute nanoindenta-

tion, pillar compression and microcantilever experiments. We investigate the effusion of deuterium and the recovery of mechanical material properties by executing experiments repeatedly after different waiting times following charging. For instance, our results have shown that the Young's modulus is not influenced by the hydrogen concentration while the hardness increases after the charging and then decreases as deuterium effuses from the metal (see Fig. 8a) [92,93]. On the other hand, the dislocation nucleation strength has the inverse relationship: the formation of new dislocations is eased in the presence of deuterium compared to the untreated and the effused sample. We investigate the dislocation avalanche probabilities in the presence and absence of hydrogen to understand thoroughly hydrogen mediated plasticity.

Simulations of fracture at the microscale: Fracture is the major process that occurs during three wear mechanisms: adhesion results in fracture from the host metal, abrasion leads to wear debris formation, surface fatigue brings about surface cracks. As such, the fundamental understanding of fracture at the microscale is essential for the solving tribology at all length scales. In collaboration with the Nano- and Micromechanics group, we execute continuum simulations to investigate the influence of the 3D stress-state on crack propagation in metals and material layer stacks. In one study [74], the influence of the elastic anisotropy and Poisson ratio on the fracture toughness along the crack front was quantified (see Fig. 8b). The experimental crack tip geometry was taken into account to determine accurately the fracture toughness and to answer fundamental questions regarding crack growth stability [75].

The delamination behaviour of metal layers is important in the integrated circuit industry, which uses four-point bending experiments to quantify the delamination strength. It had been previously observed

that these experiments are frequently unsuccessful [94,95]. Our study revealed the origin of the frequent experimental failure and the project gave design guidelines for successful experiments [96].

The project with the Boise State University, which was funded as part of the Materials-World-Network of NSF and DFG, was concluded. Our contribution investigated the conjugation boundary in hierarchical magnetic shape memory alloys and used disclination dynamics to simulate the growth of variants and material failure [94]. Our partner supported the microstructural evolution by using high-resolution TEM of a conjugation boundary and the variant evolution mechanisms.

We participated in the first and third Sandia Fracture Challenge, in which calibration experiments are used to identify the material and fracture model on the macroscale. After blind predictions are calculated for a custom 3D geometry, the experiments are used to verify the numerical predictions [97-100].

Intermetallic Materials (M. Palm, F. Stein)

The mission of the group is the development of intermetallic materials including fundamental research on phase stability and phase transformations. Based on that, alloy concepts are established and employed for designing alloys with specific microstructures and optimized compositions. If - after evaluation of basic physical and mechanical properties and the corrosion behaviour - expectancy for a successful application exists, implementation is explored in cooperation with industrial partners. The majority of the research is performed within national and international collaborations and the application-oriented projects are collaborations with industries. Projects also often involve other groups at the MPIE.

Fundamental research on phase stability and phase transformations. Nb-based intermetallic alloys consisting of Nb solid solution and high-melting, strengthening intermetallic phases are of considerable interest for structural applications at very high temperatures. In a project a company for special metals, the high-temperature phase equilibria and solidification behaviour of Nb-based ternary alloys with Al and Fe were established yielding the liquidus surface in the Nb corner of the ternary system and isothermal sections at 1450 and 1600 °C [101]. The phase relations in the complete ternary Al-Fe-Nb were calculated by thermodynamic modelling using the Calphad approach within a cooperation with Nanning University [102], and a comprehensive assessment of the complete system was performed [103].

The precipitation of intermetallic phases from a supersaturated Co(Nb) solid solution is studied in a cooperation with the Hokkaido University of Science. These ongoing investigations show that the formation of metastable, coherent $L1_2$ $NbCo_3$ strongly affects the microstructural evolution and growth of the equilibrium phase Nb_2Co_7 [104].

Deviations from the ideal, stoichiometric composition of tcp (tetrahedrally close-packed) intermetallic phases as, e.g., Laves phases can be partially compensated by point defects like antisite atoms or vacancies, but also planar defects may offer an opportunity to accommodate excess atoms. In cooperation with the group Advanced Transmission Electron Microscopy, various types of such planar faults in a Nb-rich off-stoichiometric $NbFe_2$ Laves phase were investigated by high-resolution STEM and accompanied by *ab initio* calculations (performed by the CM department) [61,62,105]. Interestingly, all types of observed planar faults contain structural motifs, which are characteristic for the crystal structure of the
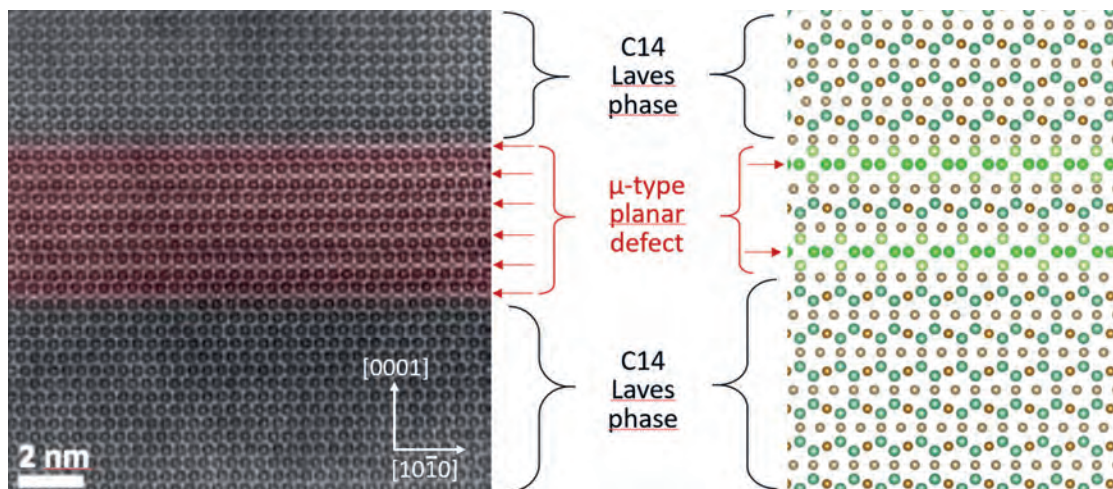
Fig. 9: *Atomically resolved STEM image of a C14-type, Nb-rich $NbFe_2$ Laves phase revealing an extended, coherent planar defect containing structural motifs marked by red arrows that are characteristic for the crystal structure of the Fe-Nb μ phase. For better visualization of the characteristic atomic arrangement in the planar defect, on the right side a magnified sketch of the structure is shown containing as an example a planar defect with two rows of the μ phase structural motifs.*

µ phase Nb_6Fe_7 that occurs at higher Nb contents in the binary system (see Fig. 9 for an example).

Multicomponent alloys with four or more principal elements in near-equiatomic ratios, commonly designated as high entropy alloys (HEAs), belong to the most discussed topics in materials science during the last years. The Intermetallic Materials group was involved in several projects dealing with various kinds of HEAs and focusing on questions related to stability and crystallographic structure of these alloys. Examples are the hexagonal HEA $Al_{15}Sc_{10}Ti_{25}Zr_{25}Hf_{25}$, where sublattice ordering resulting in a $D0_{19}$ super-structure was found below 900°C [106], and the equiatomic, hexagonal HEA YGdTbDyHo, where a hitherto unknown and still unsolved hexagonal superstructure with $P6_3$ symmetry was detected [39].

Prediction of the stability and properties of phases by *ab initio* methods is becoming more and more important for materials development. Within a cooperation with the Czech Academy of Sciences, Montanuniversität Leoben (MUL) in Austria and the SN department, thermodynamic, electronic, magnetic, structural and elastic properties of the $L2_1$ Heusler phase Fe_2AlTi have been explored [67]. The phase is interesting for functional applications because of its unusual magnetic and electrical properties but also for strengthening Fe–Al alloys at high temperature. Fe_2AlTi has an extended homogeneity range and the effect of off-stoichiometry on the magnetic states and thereby on the lattice parameter was investigated.

Alloy design. *Ab initio* results on various $L2_1$ Heusler phases contribute to the theory-guided design of novel Fe-Al-based superalloys. Such alloys have a coherent microstructure consisting of disordered $A2$ and intermetallic phases with $B2$ or $L2_1$ structure. Strength and stability of the microstructure of these alloys crucially depend on optimizing the coherency stresses between the phases. As actual alloys are developed in systems containing four or more elements, *ab initio* calculations for the prediction e.g. of the stability of $L2_1$ in such higher order systems and their lattice constants are fundamental for the design of these alloys [66].

In cooperation with the Montanuniversität Leoben and the group Advanced Transmission Electron Microscopy, we develop ferritic superalloys in the Fe-Al-Ni-Ti system [64,65]. The focus is placed on the evolution of the microstructure in dependence on different heat treatments. Specifically the coherence between the $A2$ α-(Fe,Ni,Al) matrix and the $L2_1$ (Fe,Ni)$_2$AlTi precipitates and the formation of Fe-rich anti-phase domains (APDs) was studied by TEM.

Ferritic superalloys can also be generated within the Fe-Al-Ta system. However, in contrast to the Fe-Al-Ni-Ti system, where the coherent microstructures of the structural related phases $A2 + L2_1$ form within a miscibility gap, $L2_1$ Fe_2AlTa forms metastably due to the kinetically retarded precipitation of the stable

$C14$ Laves phase $(Fe,Al)_2Ta$. Within a cooperation with industry aimed at producing compressor blades strengthened by coherent $A2 + L2_1$ microstructures, possibilities to modify the microstructure by manipulating the metastable formation of $L2_1$ by doping with boron or by a thermomechanical pre-treatment have been explored [63].

Co-Ti based ternary γ/γ' superalloys containing 12 at.% Ti and 4 at.% Cr or Mo and heat-treated at 800 °C were investigated within a cooperation with the MA department. Mo and Cr were found to preferentially occupy Ti sites in the $L1_2$ γ' phase and to lead to an increase of the γ' volume fraction, a reduction of the lattice misfit, and an increase of the γ' solvus temperature that amounts to more than 100 °C in case of the Mo-containing alloy [107].

Evaluation of basic properties. Mechanical properties of intermetallic phases may be significantly affected by changes in composition what is most obvious for phases with extended homogeneity ranges. The $NbCo_2$ Laves phase is a perfectly well suited example to study this topic as the width of its homogeneity range is about 10 at.% and it additionally may exist with three different structure variants (cubic $C15$, hexagonal $C14$ and hexagonal $C36$). As the preparation of bulk single-phase Laves phase samples for classical mechanical testing is extremely difficult for such a brittle material, an alternative production route was employed. Diffusion couples were prepared containing a concentration gradient that covers the complete homogeneity range of the Laves phase. By performing various types of micro-mechanical testing methods along the concentration gradient, the mechanical properties were studied as function of composition and structure in cooperation with the Nano- and Micromechanics group [59,60].

Al-rich Fe-Al alloys were studied in a project with the Karlsruhe Institute of Technology (KIT). After a careful re-investigation of the phase diagram in the complete Al-rich part of the system [54], the investigations focused on the two-phase range $FeAl + FeAl_2$, where the microstructure consists of a fine-scaled, well-aligned lamellar arrangement of the two phases. The orientation relationship of cubic $B2$ FeAl and triclinic $FeAl_2$ was determined [55] and the coarsening kinetics of the lamellar microstructure were studied in detail [56]. In view of possible applications, creep experiments between 600 and 800 °C were performed on respective alloys [57] and the effect of ternary additions of up to 2 at.% B, Ti, Cr, Cu and Mo on the lamellar microstructure, their thermal stability and mechanical properties was investigated [58].

Coherent $A2 + D0_3$ ($L2_1$) microstructures as observed in the above-mentioned Fe-Al-Ni-Ti and Fe-Al-Ta systems also form in the Fe-Al-V system. The investigated alloys show appreciable mechanical properties, but their oxidation behaviour is imperfect due to the formation of porous and thick Fe_2O_3 +

Al_2O_3 scales [44]. Besides ferritic superalloys, iron aluminides with boride precipitates are of high interest in view of industrial applications. Fe-Al-Nb-B alloys with finely precipitated Laves phase show increased ductility after heat treating but only mediocre creep resistance [45].

Because systematic investigations on the variation of fundamental properties of iron aluminides in dependence on the Al content are missing, respective investigations have been performed over the years at the MPIE. Currently the oxidation [46] and the aqueous corrosion behaviour [47,48] are studied, the latter in cooperation with the GO department. X-ray photoemission spectroscopy (XPS) revealed that passivation during wet corrosion is due to the formation of an outer layer of mixed Al and Fe oxides and an inner layer of hydroxides enriched in Al.

Implementation into industrial application. Mechanical properties and corrosion behaviour of the Fe-Al-based alloys discussed above were evaluated in cooperation with industry partners. Besides optimizing or finding alternative intermetallic materials, these projects are aimed at producing and testing parts fabricated by various processing routes. Specifically, a number of different parts for ship diesel engines, industrial furnaces or steam turbines were cast or forged using boride containing iron aluminides and in several cases successfully tested under application conditions [49].

Additive manufacturing (AM) is a new technology by which near net-shape parts are generated by layer-wise melting of powders by a laser or electron beam. As intermetallic phases are highly wear resistant and therefore difficult to machine, AM is an interesting alternative for producing parts from intermetallic materials. Within a large-scale collaboration with research institutes and German industries, AM of advanced iron aluminides has been studied. Defect-free samples and parts were produced by different AM techniques and it was shown that ba-

sic alloy concepts developed for cast alloys can be transferred to AM [50-52]. Also, the possibility of generating chemically-graded samples by AM with a continuous variation of the composition between various stainless steels and iron aluminides could be demonstrated [53].

In recognition of the substantial research at the MPIE, invitations have been offered to write a review on iron aluminides [108] and a book chapter on Fe-based intermetallic phases [109]. The group is also active in co-organizing the bi-annual conference Intermetallics (https://www.intermetallics-conference.de/), the annual MSIT Winter School on Materials Chemistry dealing with heterogeneous equilibria (http://www.msiport.com/msit-school/) as well as the international workshop on Laves phases at the MPIE.

Synthesis of Thin Films and Nanostructured Materials (G. Dehm, since Nov. 2018 M. Ghidelli)

This group was recently established with the aim to synthesize specific thin film microstructures and nanostructured thin film materials. The new group leader Dr. Matteo Ghidelli was attracted from Politecnico di Milano and complements with his expertise on physical vapour deposition techniques and microfabrication processes the research portfolio of the SN. While the head of this new research group started just recently, some studies in this research field had been already initiated earlier and were often performed jointly with the groups Nano- and Micromechanics of Materials, Advanced Transmission Electron Microscopy and/or the Max Planck Fellow group on Self Reporting Materials. Examples include new insights on solid state dewetting of thin films with oxide scale, which was studied in close collaboration with the independent research group Nanoanalytics and Interfaces (NG, head: Prof. C. Scheu). Epitaxial Al films on sapphire were dewetted in reducing and oxidizing atmospheres providing clear indication of the different diffusion paths being
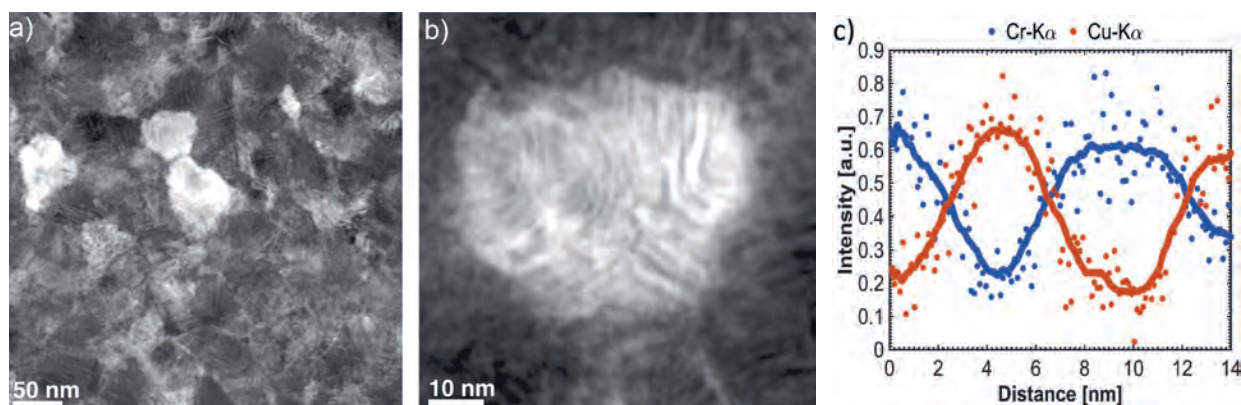
Fig. 10: *STEM Z-contrast images showing (a) the nanocrystalline structure of a bcc Cu-Cr alloy (67 at.% Cu, 33 at.% Cr) and (b) the chemical modulation within an individual grain (taken from [36]), (c) shows an EDX linescan within a single grain.*

activated [5,6,110]. Such studies are not only relevant for functional devices with their thin metallization layers but also for thin passivating coatings on alloys enduring long exposures to elevated temperatures. Another example of intensive research is the fabrication, structure evolution and thermal stability of alloy nanocomposites in form of thin films. Recent studies revolved mainly around the system Cu-Cr, where thin film structures [3,4,35-37] and severe plastically deformed bulk materials [1,7] were analysed. Thermal stability against grain growth with excellent strength is achieved in Cu supersaturated bcc Cu-Cr alloys, where spinodal decomposition via volume diffusions leads to a hierarchical nanostructure of chemically modulated layers within nanocrystalline grains (Fig. 10) [36,37]. These first studies indicate the potential of thin films to tailor nanostructures and to provide selection guidelines for upscaling to bulk materials via other synthesis techniques like rapid solidification or severe plastic deformation. This research path will be further explored for other material systems in the upcoming years.

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Research Projects in Progress

ERC Grant (G. Dehm)

Bishara, Meiners, Saba, Kirchlechner, Liebscher, Dehm: Correlating the State and Properties of Grain Boundaries

Nano- and Micromechanics of Materials (C. Kirchlechner)

Arigela, Kirchlechner, Dehm: Setup of a microscale high-temperature loading rig

Balijepalli, Kirchlechner: StrengthSwitch: Can we design structural materials with switchable strength?

Du, Kirchlechner, Dehm: Micro-fracture of advanced solder joints

Li, Kirchlechner: Dislocation source activation at grain boundaries

Kini, Kirchlechner, Dehm: The role of microstructure constraints during slip transfer

Kirchlechner, Fink, Kirchlechner, Dehm (in cooperation with J. Schneider, RWTH Aachen): Fracture behavior of metallic glass thin films

Kumar, Brinckmann, Kirchlechner, Dehm: Developing strategies for reliably assessing elasto-plastic fracture mechanics

Kumar, Kirchlechner (in cooperation with A. Kumar and M. Herbig, MA-Department): Fracture toughness of a white etching layer

Malyar, Hosseinabadi, Dehm, Kirchlechner: Slip transfer through grain boundaries

Molin, Renversade, Kirchlechner (in cooperation with J.S. Micha, CEA Grenoble): The first stages of fatigue

Öllers, Arigela, Kirchlechner, Dehm (in cooperation with A. Ludwig, RUB Bochum): Combinatorial approach to tailor electrical and mechanical properties of alloyed thin film structures

Seok, Kirchlechner, Dehm (in cooperation with S. Nandy, S. Zaefferer and D. Raabe, MA-Department): The anisotropy of the CRSS in Mg alloys

Tian, Christiansen, Kirchlechner (in cooperation with D. Ponge, MA-Department): Damage initiation in DP800 at the micron scale

Wenqi, Kirchlechner, Liebscher, Dehm: The strain-rate-sensitivity of high-entropy alloys

Advanced Transmission Electron Microscopy (C. Liebscher)

Ahmadian, Liebscher, Dehm (in cooperation with L. Romaner, Materials Center Leoben, Austria): Atomic structure, transitions and segregation effects in bcc grain boundaries

Devulapalli, Dehm, Liebscher: Structural transitions and atomic scale segregation effects in Ti alloy grain boundaries

Jeong, Brinckmann, Liebscher, Dehm: In situ TEM nanotribology

Jenko, Dehm, Liebscher: *In situ* TEM observation of dynamics and growth characteristics in bi-metallic Fe-Au nanoparticles

Lee, Duarte, Soler, Kirchlechner, Liebscher, Dehm (in cooperation with M. Feuerbacher, FZ Jülich, Germany and S. Ho Oh, Sungkyunkwan University, Republich of Korea): *In situ* TEM study on the dislocation plasticity in a single crystal FeCoCrMnNi high entropy alloy

Lee, Meiners, Dehm, Liebscher: Atomic scale *in situ* TEM investigations of dislocation grain boundary interactions

Liebscher, Stein (in cooperation with A. Zendegani, T. Hickel, CM-Department; M. Šlapáková, Charles University in Prague, Czech Republic and S. Kumar, Brown University, USA): Atomic scale transitions at planar defects in $C14$ $NbFe_2$ Laves phases

Liebscher (in cooperation with A. Kauffmann and M. Heilmaier, Karlsruhe Institute of Technology, Germany): Nanoscale phase separation and ordering tendencies in refractory MoCrTiAl high entropy alloys

Liebscher, Dehm (in cooperation with C. Draxel and C. Koch, Humboldt University Berlin, Germany): Development of data structures and metadata for big datasets in multidimensional scanning transmission electron microscopy

Liebscher (in cooperation with C. Freysoldt, MA-Department; A. Ziletti and L. Ghiringelli, Fritz-Haber Institute Berlin, Germany): Automatic classification and feature extraction from multi-dimensional TEM data

Lu, Meiners, Liebscher, Dehm, Raabe (in cooperation with L. Morsdorf, M. Herbig, A. Breen, MA-Department; R.K.W. Marceau, Deakin University, Australia): Phase decomposition in lenticular martensite during room temperature ageing

Lu, Liebscher, Raabe, Dehm, Gault (in cooperation with Y. Chang, A. Breen, I. Mouton, D. Raabe, B. Gault, MA-Department): Hydride formation mechanisms in Ti alloys

Lu, Liebscher (in cooperation with A. Breen, I. Mouton, Z. Wang, A. Szczepaniak, P. Kontis, L. Stephenson, Y. Chang, A. Kwiatkowski da Silva, D. Raabe, M. Herbig, B. Gault, MA-Department; S. Wang and T. Britton, Imperial College, UK): Atomic scale analysis of deuterides in Zircaloy-4

Lu, Liebscher, Dehm (in cooperation with Z. Li, D. Raabe, MA-Department): Atomistic deformation mechanisms and nanolaminate formation in dual-phase high-entropy alloys

Lu, Liebscher, Dehm (in cooperation with Z. Li, D. Raabe, MA-Department): Phase formation and deformation mechanisms in interstitial dual-phase high entropy alloys

Meiners, Dehm, Liebscher (in cooperation with T. Frolov, Lawrence Livermore National Laboratory): Atomic scale phase transitions at [111] tilt grain boundaries in Cu

Peter, Kirchlechner, Liebscher, Dehm (in cooperation with T. Frolov, Lawrence Livermore National Laboratory, USA and C. Ophus, Lawrence Berkeley National Laboratory, USA): Segregation induced nanofacet formation at asymmetric Cu grain boundaries

Peter, Kirchlechner, Liebscher, Dehm: Correlating the atomic structure of grain boundaries in Cu with their dislocation interaction behavior

Wolff-Goodrich, Dehm, Liebscher (in cooperation with M. Amalraj, RWTH Aachen, Germany and K.G. Pradeep, IIT Madras, India): Tailored, precipitation strengthened, compositionally complex FeAlCr (Mn, Co, Ni, Ti) alloys for high temperature applications

Wu, Liebscher, Dehm (in cooperation with S.K. Makineni, P. Kontis, B. Gault, D. Raabe, MA-Department; G. Eggeler, Ruhr-University Bochum: Segregation effects to dislocations and stacking faults in the γ'-phase of single crystal Ni-based superalloys

Zavasnik, Dehm, Liebscher: In situ TEM deformation of metastable Cu-Ag thin films

Zavasnik, Dehm, Liebscher: Atomic scale defect healing in acusto-optic $PbMoO_3$ single crystals

Nanotribology (S. Brinckmann)

Brinckmann: Blind predictions of plasticity and failure of additively manufactured metals (together with B. Boyce, Sandia National Labs)

Brinckmann, Dehm: Tribolayer formation during macro- and microscale cyclic contact (in collaboration with G. Jacobs, RWTH Aachen)

Brinckmann, Dehm (in cooperation with C. Greiner, KIT and R. Chromik, McGill University): Tribology of Cu on the macro- to microscale

Brinckmann, Kirchlechner, Dehm (in cooperation with M. Bartosik and P. Mayrhofer, TU Wien): Designing toughening concepts for future hard coatings

Brinckmann, Soler, Dehm: Shear experiments to determine the delamination strength of thin-films

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

Duarte Correa, Dehm: Corrosion and wear at the nanoscale

Fang, Brinckmann, Dehm: Hydrogen embrittlement of steels: environment-assisted *in situ* micromechanical tests

Farzam, Brinckmann, Dehm: Microstructure evolution in Cu and Al during friction

Fink, Brinckmann, Dehm: Microstructure evolution of pearlitic steel during nanotribology

Patil, Brinckmann, Dehm: Texture evolution during nanotribology in FCC and BCC steels

Rao, Duarte Correa, Dehm: Hydrogen-microstructure interactions in Ferritic alloys at small scale

Xia, Brinckmann, Dehm: Fracture initiation in FCC and BCC metals during tribology

Intermetallic Materials (M. Palm, F. Stein)

Distl, Kahrobaee, Palm, Stein (in cooperation with Thermo-Calc Software AB, Sweden, Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung GmbH, Montanuniversität Leoben, Austria): ADVANCE – Sophisticated experiments and optimisation to advance an existing CALPHAD database for next generation TiAl alloys

Jenko, Palm: TEM investigation on boride precipitation in iron aluminides

Liebscher, Stein (in cooperation with A. Zendegani, T. Hickel, CM-Department; M. Šlapáková, Charles University Prague, Czech Republic, S. Kumar, Brown University, RI, USA): Planar defects in off-stoichiometric, Nb-rich $NbFe_2$ Laves phase studied by HRTEM

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

Merali, Stein: Diffusion couple studies on the possibility of coexistence of hexagonal and cubic Laves phases in the Co-Ti system

N.N., Palm, Stein (in cooperation with Siemens AG, Karlsruher Institute of Technology, Otto Junker GmbH, Rolls-Royce Deutschland Ltd & Co KG, Access e.V., Leistritz Turbinentechnik GmbH): Pro-FeAl – Process development for economic and efficient iron aluminide turbine components

Palm (in cooperation with P. Kratochvil, V. Sima, Dept. Physics of Materials, Charles University Prague; P. Hanus, M. Švec, Technical University Liberec, Czech Republic): Basic investigations of iron aluminide alloys including phase formation during infiltration

Palm (in cooperation with I.G. Aviziotis, M. Armbrüster, Technical University Chemnitz): Synthesis and characterization of iron aluminide catalysts

Palm, Stein, Liebscher (in cooperation with F. Godor, S. Mayer, H. Clemens, Montanuniversität Leoben): Development of Fe-Al materials with coherent microstructures (ferritic superalloys)

Peng, Palm (in cooperation with Winterthur Gas & Diesel Ltd.; Wärtsila Finland Oy; Wärtsila Netherlands BV; Deloro Wear Solutions GmbH; ABB Turbo Systems AG): Intermetallics for engine applications (within HERCULES-2)

Stein (in cooperation with S. Takajo, S. Vogel, Los Alamos National Lab, NM, USA): High-temperature phase transformation of Hume-Rothery-type phases in the Fe-Al-Mo system

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

Stein (in cooperation with K. Yamada, T. Horiuchi, Hokkaido University of Science, Japan): Metastable $L1_2$ phase formation in Co-Nb alloys

Stein (in cooperation with R. Sandt, University of Cologne, R. Spatschek, Forschungszentrum Jülich): Experiments and modelling on the reaction kinetics of the peritectoid decomposition of Nb_2Co_7

Stein, Palm (in cooperation with R. Wartbichler, S. Mayer, H. Clemens, Montanuniversität Leoben, Austria): Experimental investigations of the effect of Mo-additions on microstructure, thermal stability and mechanical properties of Ti-60Al alloy