Part II.

The departments

Department of Computational Materials Design (CM)

J. Neugebauer

Scientific Objective and Department Structure

The research activities of the department Computational Materials Design rest on three pillars: (i) **development** and implementation **of advanced *ab initio* guided methodologies and algorithms**, (ii) **application of these tools** to address **fundamental materials science questions**, and (iii) utilization of these insights to **explore and identify novel strategies in materials design** and synthesis. Based on these pillars fundamental mechanisms controlling the microstructure, the properties and the synthesis of a wide variety of materials, ranging from metallic alloys over semiconductors for optoelectronic and high-power electronics to electrochemical systems, could be – often in close collaboration with our experimental partners at the MPIE – successfully studied.

In the reporting period several major successes have been achieved: Our **recent developments in advanced numerical/physical algorithms, machine learning and automated workflows** opened the opportunity to study structurally and/or chemically complex materials systems that were until recently out of reach for *ab initio* based simulation methods. Examples are **compositionally complex materials** consisting of four or more chemical species [1-14; see p. 210, p. 194, p. 208], **electrochemical interfaces** as relevant for corrosion or energy conversion [15-18; see p. 224, p. 69, p. 198], the structural, mechanical and chemical interplay at crystal defects resulting in **defect phases** [19-24; see p. 192, p. 196, p. 206] and the impact on **mechanical properties** [25-27; see p. 194] and the mechanisms controlling the **resolution and interpretation of advanced experimental techniques** such as, e.g., atom probe tomography (APT) [28-31].

Many of these applications became only possible by systematically extending our in-house developed **materials science integrated development platform pyiron** [www.pyiron.org; see p. 72; 32-36]. In the last three years pyiron has evolved as a highly efficient tool that provides and combines all steps occurring in the development and application of our advanced simulation techniques. The expertise gained by developing pyiron as well as its rapid prototyping, data handling and high performance computing capabilities brought the department into an ideal position to **successfully initiate and join large scale digitalization projects in industry and academia**. Examples are the **National Research Data Infrastructure (NFDI)** initiative (see p. 81), which aims to establish a unified research data infrastructure for universities and academic research organizations, or the **Platform MaterialDigital** (see p. 80), which wants to provide such an infrastructure for industry. It also helped to establish large scientific networks such as the **Collaborative Research Centre on defect phase diagrams** (see p. 76) by providing the necessary data and workflow infrastructure. Many of the scientists working in these projects are highly active in the further development of pyiron. They formed a board of core-developers that together with external developers outside MPIE introduces, supervises and directs the implementation of new features, simulation tools and ontologies.

This newly developed **expertise in big data analytics, machine learning and software engineering** made the department attractive for scientists interested in combining this expertise with materials science concepts and changed partly its scope and composition. It also allowed the department to **successfully extend the powerful concepts developed in previous years**. Examples are the extension on the fully *ab initio* computation of key thermodynamic quantities such as free energies **from unaries to compositionally complex alloys** [19-20, 27, 37-45], the **transition of labour intensive computations into a fully automated approach** to determine precise melting temperatures [36], a correction schema to enable accurate *ab initio* calculations of the technologically highly relevant class of semiconductors exhibiting spontaneous polarization [46], or to model the impact of the extreme electric fields occurring in atom probe tomography [28, 47].

Utilizing machine learning concepts together with the above simulation techniques also opened a new class of **joint activities with the other departments to boost experimental resolution and interpretation**. For example, these techniques have been successfully used to achieve **chemical resolution for field ion microscopy** (FIM) measurements (see p. 220), to **reveal solute-vacancy interaction in APT** [29] or to design a **fully automated segmentation algorithm** for atomic resolution microscopy [30].

The rapid prototyping capabilities, the interactivity of pyiron, and the ease to create automated workflows also enabled the department to **develop and implement new group activities to handle the restrictions imposed by social distancing measures** due to the COVID-19 pandemic. The traditional department retreat was replaced in 2020 by a three-day hackathon, where small groups consisting of 3-6 scientists were identifying challenging materials science simulation topics and were jointly developing, coding, and testing algorithms and tools in interactive sessions. This first hackathon was so successful, that many of the participants proposed to make this a regular event. As a result, 3-5 groups with changing participants organize weekly two-hour **hackathons** on various topics, where members of the department **develop, program and discuss new simulation tools and algorithms** (see p. 216). Also, based on the success and the grass-root organization of these meetings a **Journal club** has been established, in which key ideas of selected publications are not only discussed, but actually implemented and tested. The highly interactive character of these meetings, enabled e.g. by Jupyter notebooks and pyiron, helped us tremendously in **integrating new members of the department** when home-office was enforced.

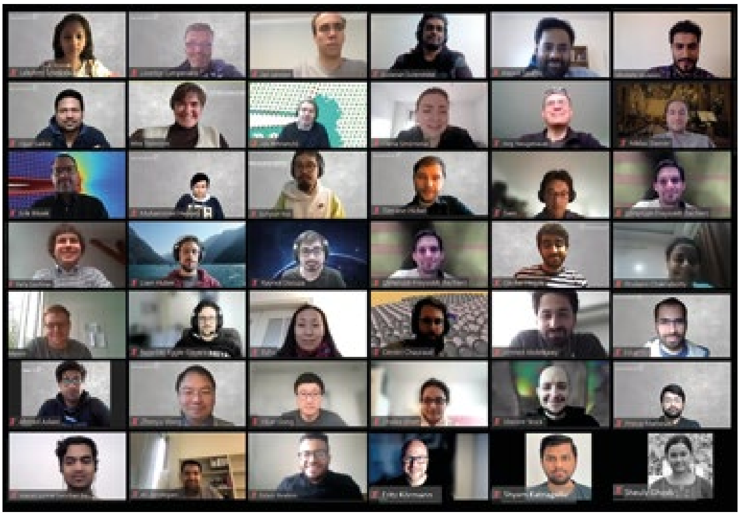

Fig. 1: *The CM department (2021)*

Many of the breakthroughs achieved in method development [15-17, 46-60], application [52, 61-71] or design [72-83] became only possible by **combining the individual expertise developed by the groups** in the department. Examples are the development of algorithms that combine spin-constraints and highly efficient atomic relaxation techniques (**Freysoldt group**) with high-performance statistical *ab initio* thermodynamics sampling approaches (**Grabowski and Hickel groups**). These algorithms and techniques are implemented in pyiron (**Hickel and Huber groups**) and applied to complex materials such as high-entropy alloys (**Körmann group**; see p. 55) or defects/surfaces and their phases (**Hickel, Huber, Lymperakis, and Todorova groups**). Also, combining the individual group expertise resulted in powerful new concepts and simulation tools, allowing to **extend available DFT** (density functional theory) **codes such that they describe a new level of physics and phenomena**. Examples are the development of a **thermopotentiostat** to realistically model the impact of extreme electric fields present at electrochemical interfaces (Wippermann (GO), Freysoldt and Todorova groups), a new approach to **boost size convergence for materials exhibiting spontaneous polarization** or piezoelectricity (Todorova and Lymperakis groups) or to **describe atomistic and electronic structure phenomena occurring at cutting edge experiments and that impact their resolution** (Freysoldt in collaboration with Gault (MA) and Liebscher (SN) groups).

The high international visibility of these developments and studies opened **prestigious job opportunities** for several members of the department. The head of the "*Ab initio* Thermodynamics group" and ERC Starting Grant Awardee (see p. 51) **B. Grabowski**, accepted a professorship position at the University of Stuttgart in 2019. **L. Lymperakis**, who is heading the group "Growth Modelling" received a professorship position at the University of Crete. **T. Hickel**, head of the "Computational Phase Studies" group, accepted a position as division head at the Federal Institute for Materials Research and Testing, BAM. To strengthen the collaborations and links between BAM and MPIE, with a particular focus on digitalization topics and large scale networking projects (see p. 80 & 81), he holds now a 50% position at both MPIE and BAM. **S.-H. Yoo** successfully applied for an Energy for Future (E4F) Postdoctoral fellowship – an initiative of the Horizon 2020 MSCA-COFUND Programme – to go to Imperial College London. **J. Janssen**, the lead developer of pyiron, graduated with distinction (summa cum laude) and started a PostDoc position at Los Alamos National Lab.
In the last period **two new groups have been established**: **L. Huber started in 2019 a group on the "Thermodynamics and Kinetics of Defects"** (see p. 41). In Fall 2021**, E. Bitzek**, formerly professor at the University of Erlangen-Nürnberg, **established a new W2 group on "Microstructure & Mechanics"** (see p. 37). His expertise e.g. in large scale atomistic simulations, fracture mechanics and mesoscale approaches ideally complements the electronic structure and atomistic expertise already existing in the department and opens exciting new links to the other MPIE departments as well as to external collaboration partners.

To foster collaborations with leading experts worldwide, members of the department actively engaged in **initiating and organizing international workshops and symposia**. Due to the Corona restrictions many of these were online workshops: Examples are two hands-on workshops utilizing pyiron. In one workshop with more than 250 participants it was shown how atomistic free energy calculations can be combined with CALPHAD concepts to obtain phase diagrams. Another hands-on workshop with ~100 participants was used to demonstrate all steps necessary to generate modern machine-learning potentials. Also, our successful biannual workshop series on "*Ab initio* Description of Iron and Steel" (ADIS; T. Hickel) took place in November 2020. C. Freysoldt was co-organizer of the BiGmax summer school, a MPG funded initiative to boost machine learning concepts in materials science. Furthermore, several symposia at international conferences like

Fig. 2: *The last in-person retreat of the CM department took place in October 2019 in Domburg (NL) with participation of colleagues from ICAMS and the TU Delft.*

the DPG (J. Neugebauer, F. Körmann, M. Todorova) and MSE (L. Huber) were organised. M. Todorova organized in Spring 2021 a virtual retreat together with partner groups at ICAMS (Ruhr-Universität Bochum) and Delft university consisting of presentations and interactive hands-on sessions. (see p. 247).

The high quality and visibility of their research enabled members of the department to receive **highly competitive and prestigious research grants**. **Z. Wang** received a FP-RESOMUS Postdoctoral Fellowship. **M. Todorova** was awarded with the Boost! Programme of the MPG that provides substantial funding and resources to propel the carrier of MPG group leaders. **S. K. Bavajigari** received a Humboldt Fellowship in Fall 2021.

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**. **T.Hickel** and **E. Bitzek** are heading the **NFDI-MatWerk Task Areas “Workflows and Software Development” and “Materials Data Infrastructure”**, respectively. **T. Hickel** and **J. Neugebauer** are Members of the **Platform MaterialDigital Steering Committee**. J. Neugebauer also served as an elected member of the DFG review board (Fachkollegiat) Materials science (until Summer 2020) and was elected into the supervisory board of the Karlsruhe Institute of Technology (KIT). Together with G. Eggeler (Ruhr-Universität Bochum) he is also **the speaker of the new Max Planck Research School on Sustainable Metallurgy (SusMet) starting in Jan. 2022** (see p. 74).

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, being directly related to many technologically relevant properties and processes in metals. Over the last three years, the group made again substantial progress in developing methods and applying them to advanced material systems. This applies in particular to the following fields of research:

- The desire to push ab initio thermodynamics to its limits, to resolve, for example, the coupling of thermodynamic, chemical and mechanical degrees of freedom, the stabilization of structural modulations, the life time of quasiparticles, or hitherto unclear features in experimental data.
- The prediction of phase stabilities next to extended defects, such as grain boundaries, stacking faults and interfaces.
- 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.
- The development of generalized workflow solutions that make the simulations in the above-mentioned fields transparent and reproducible.

The research in the group is more and more characterized by digitalization strategies within the department and well beyond. The main motivation for the group is to convey the innovative methodological developments from one project to the other and to provide a flexible environment that allows a quick adaptation to new ideas and concepts. The integrated development environment (IDE) pyiron is ideally suited for this purpose. Its philosophy and success have already been outlined before (see

p. 72). Particularly relevant in the context of the group is the deployment for the complex simulation protocols required for ab initio thermodynamics.

One of the fundamental concepts of pyiron is to consider data and workflows as a unity. In this way the FAIR (findable, accessible, interoperable, reusable) data policies, which are pushed forward by national and international consortia, are automatically fulfilled. The philosophy of pyiron is, therefore, a cornerstone of large-scale national initiatives like Platform MaterialDigital (see p. 80) and NFDI MatWerk (see p. 81).

To ensure the sustainability of the digitalization activities the group head (T. Hickel) received the offer to start a second employment at the BAM Federal Institute of Materials Science and Testing. His intention is to establish another centre for the development of workflows in materials science at a place that has the strategic mission of the government to ensure standards, quality, and safety in materials science. At the same time, BAM offers the opportunity to spread the developed digitalization concepts within one institution to a large number of stakeholders from different disciplines in materials science, including multiscale simulations and experiment, but also the interface to chemistry and engineering. BAM has the potential to give Platform MaterialDigital, NFDI-MatWerk and the workflow solutions therein a long-term perspective and operation centre, well beyond the funding period of these initiatives. In order to build up these new scientific and strategic developments at BAM, T. Hickel had to reduce his employment and time budget at MPIE to 50%, starting from 1 August 2021. Altogether, a substantial part of the group resources in the last three years has been invested in these digitalization activities.

In the field of ab initio thermodynamics, the previous achievements in handling all entropy contributions to the Gibbs free energy with highest-possible accuracy have been used to investigate the coupling of different degrees of freedom. One highlight was the prediction of phonon lifetimes, resulting from the interaction of phonons with other phonons [48], with chemical disorder [60], and with magnetic disorder [37] (A. Glensk, B. Dutta). These studies emphasize the dominance of local effects such as the anharmonicity of local pair interactions [48] as well as fluctuations of the local chemical environment [60]. The consideration of local magnetic fluctuations has revealed that the assumptions of a spin-space averaging approach are for realistic materials and time scales sufficient, to describe their phonon spectrum [37] (B. Dutta).

Our approaches in ab initio thermodynamics have strengthened the ab initio guided calculation of phase diagrams. As part of the efforts towards a third generation of Calphad databases, novel concepts for a parametrization of the solid phase beyond the melting point have been investigated for Al alloys [38] (A. Glensk). Furthermore, an assessment of magnetic models has been performed by a comparison with ab initio based Monte-Carlo simulations for hard-magnetic materials [72] (H. Sözen) and the applicability of empirical rules has been tested such as Neumann-Kopp in a temperature regime where anharmonic vibrations are relevant [39] (A. Gupta). Recently, thermodynamic approaches have been applied to predict the stability of chemically complex carbides (L. Sreekala). In addition, the thermodynamics of binary Fe-Mn alloys has been extended to machine learning approaches to handle the complexity of magnetic interactions in metallic alloys [62] (O. Waseda).

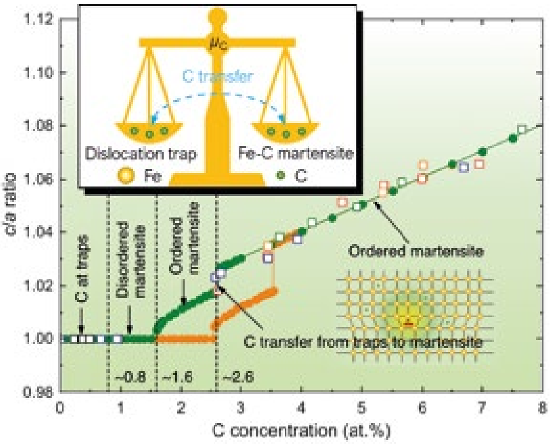

Fig. 3: *Comparison of experimental (open squares) and theoretically computed (filled circles) c/a ratio of Fe-C alloys as a function of C concentration at room temperature. Calculations with (green circles) and without (orange circles) considering anharmonicity have been compared. Figure adapted from [26].*

The thermodynamics of defects is a third major topic of the group that substantially gained importance after the establishment of the CRC1394 “Structural and chemical atomic complexity” (see p. 76). The extension of the concept of bulk phase diagrams to defect phase diagrams is one of the major visions of these activities [19]. Substantial breakthroughs in the development of these concepts have been achievement in the context of stacking faults in an off-stoichiometric Fe_2Nb Laves phase [20] (A. Zendegani). We have transferred the established convex hull representation to a phase diagram as a function of chemical potentials and have included the coherency strain as an additional degree of freedom (see p. 192). These concepts are currently extended to other material systems such as Mg alloys (A. Tehranchi, P. Mathews) and Al alloys (P. Chakraborty, A. Aslam).

The thermodynamics of defects in magnetic materials is particularly challenging due the different time scales of magnetic fluctuations and atomic relaxations. Taking this properly into account, has a substantial impact on the atomic relaxation next to vacancies and therefore the vacancy formation and migration energies [40]. The decisive role of planar defects has also been investigated in magnetic materials, where the presence of twin boundaries has been found to substantially reduce the size of magnetic domains in MnAl Heusler alloys [63] (O. Hegde).

Several investigations have again been devoted to mechanisms in structural materials. One of the outstanding findings, is related to the competition between interstitial ordering in Fe-C alloys and the segregation to extended defects such as dislocations (Fig. 3). We have predicted an effective decrease of this segregation for high interstitial concentrations, which was confirmed by atom probe tomography [26]. Other works are related to the kinetics in these materials as, for example, the multicomponent interdiffusion in Ni-Al alloys [60]. The research on hydrogen embrittlement of structural materials was boosted by an European RFCS grant on the "Hydrogen interaction with retained austenite under static and cyclic loading conditions" that is coordinated by T. Hickel. One outstanding finding within this project is the change of phase stabilities due to the presence of hydrogen (A. Tehranchi). Similarly, the interplay of hydrogen with carbides in steels has been investigated (L. Sreekala, Fig. 4). A fruitful collaboration with the group of B. Gault within the ERC project SHINE (see p. 50) has led to amazing insights into the competition of precipitates and grain boundaries in the hydrogen embrittlement of Al alloys (P. Chakraborty).

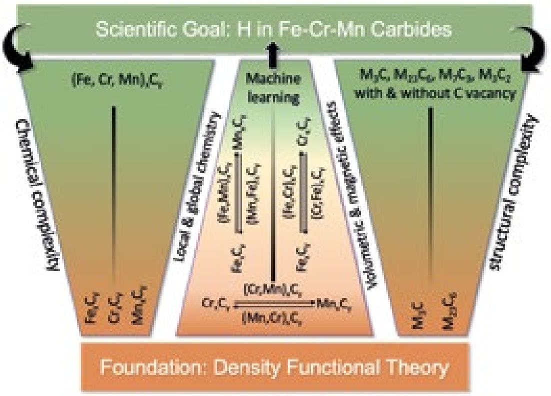

Fig. 4: *Research strategy for exploring chemical trends in the solubility of H in complex Fe-Cr-Mn carbides taking the chemical and structural complexity into account. The employed machine-learning approach is based on fundamental insights obtained from density functional theory.*

The computational design of functional materials was on the one hand devoted to hard-magnetic alloys. Using the example of $CeFe_{11}Ti$ revealed that the high-throughput optimization of certain key descriptors needs to be combined with an analysis of the phase stability of these alloys [45]. Based on these insights, we have analysed in an upcoming work, how this stability can be influenced by alloying elements (H. Sözen). On the other hand, a similar approach has been applied to Fe-based superconductors. Here, the delicate interplay of magnetic and van-der-Waals interactions have been used to describe the structural stability and the consequences for superconductivity in FeSe alloys [49]. This provided us the chance to systematically explore the impact of alloying elements such as S and Te on these properties (F. Lochner). In this way, we were able to demonstrate the relevance of our thermodynamic methods for novel materials and innovative applications.

Defect Chemistry and Spectroscopy (C. Freysoldt)

The group "Defect Chemistry and Spectroscopy" works on atomic-scale simulations of electrical charging phenomena by means of ab initio methods, and develops state-of-the-art methods and concepts for this purpose. Additionally, the group is growing towards machine-learning from the rich data sets produced by the key experiments at MPIE, notably electron microscopy and atom probe tomography.

The performance of functional energy materials - optoelectronics, solar cells, power electronics, batteries etc. - is intimately linked to where the electrical charges are stored at the atomic scale, and which processes are enabled or hindered at the relevant sites. Ab initio electronic structure theory is the decisive work horse for predictive simulations, but very challenging in practice due to the coupling of electronic effects at the local scale with macroscopic fields created far away, or artificially introduced by the modelling approach. While the group had long concentrated on the role of point defects in bulk materials, this has been gradually broadened to include surface- and interface effects, which are often of central importance in devices. This long-standing expertise is shared with other groups (Todorova, Wippermann) to support their innovations in electrochemical simulation techniques [15; see p. 69].

In the area of point defects, the group engages in various international collaborations. The recently developed charge correction scheme for surfaces and interfaces [50] has enabled investigations of defects in 2D materials in collaboration with R. Hennig (University of Florida), notably in MoS_2 [65]. Based on an initiative by Y. Kumagai (Tokio Institute of Technology), the charge correction scheme for bulk defects was further extended to vertical excitations in ionic materials [51]. The group's reputation is further underlined by the fact that several students from abroad recently secured funding for short- and long-term visits, which will take place once the pandemic situation permits.

The simulations of surfaces under extreme electric fields, such as encountered in atom probe tomography (APT) or field ion microscopy, have now been firmly established. M. Ashton, Alexander von Humboldt awardee, not only revealed a field-controlled two-stage evaporation path in field evaporation [28] (Fig. 5), but also addressed the puzzling behaviour of H in APT. The group maintains close bonds to the experimental APT group (B. Gault) and aims at deepening the understanding of field evaporation mechanisms from a DFT perspective (S. Katnagallu, since July 2021), as well as establishing an ab initio theory of field ion microscopy (S. Bhatt, PhD student since May 2021).

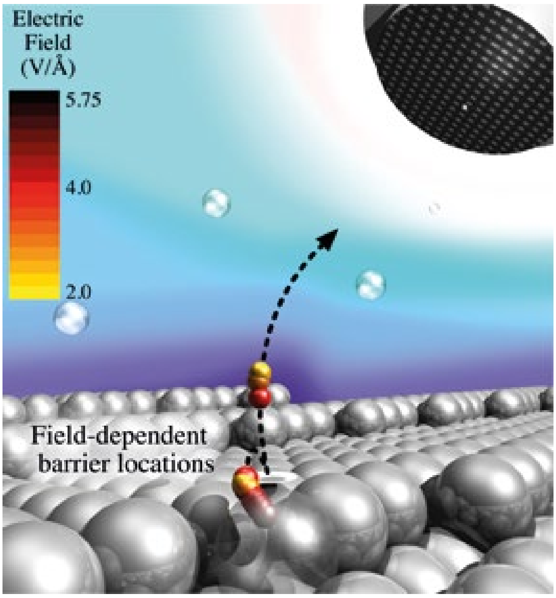

Fig. 5: *Visualization of field-controlled two-stage field evaporation paths of tungsten [28]. The red balls visualize the barrier position at different applied fields. A kink site atom may first roll up the step (lower set of barriers), and then evaporate from the step-position (upper part). At fields above 4 V/Å, the upper barrier vanishes and the kink atom undergoes direct evaporation from its original position.*

All these method developments would not be possible without the SPHInX package [84] as the code framework, which continues to be enhanced by the group. In addition to strengthening the integration with pyiron to exploit the latest features of the SPHInX DFT code, a complete rewriting of the algebraic core classes and partial reorganization of the physics code base has been undertaken in 2020 to overcome existing limitations, improve the maintainability, adopt a modern C++ standard, and simplify future extensions. This was released as SPHInX 3.0. In this context, significant efficiency gains for the k.p module could be realized (collaboration with O. Marquardt, Weierstraß-Institut Berlin).

As a new direction, triggered by the Max Planck network on Big-data driven material science (BiGmax, see p. 82), the group has started to explore machine-learning from the huge experimental data sets produced in electron microscopy and atom probe tomography. The unique opportunities coming from data-rich, yet noisy experimental signals that exhibit recurrent, but fuzzily defined patterns will require automated analysis tools that exploit material science domain knowledge. In electron microscopy (see p. 222), an efficient and robust segmentation of atomic-resolution images and videos, based on crystal symmetry descriptors was developed (N. Wang) [30]. Moreover, by adopting the idea of physics-informed neural networks it was demonstrated that a coarse-grained, very compact phase-field representation can be extracted from in-situ STEM time series (video sequences) of phase transformations and evolution (N. Wang, now L. Sreekala).

These activities have been further extended in the framework of the newly established Helmholtz Data Science School for Life, Earth, and Energy (HDS-LEE), which MPIE has joined as a partner institution. Embedded in the institute's strategy to push forward sustainable metallurgy, the first project aims at designing scrap-compatible Al alloys to increase the fraction of recycled Al, thus leveraging CO_2 emission from Al production from primary sources. The fate of unintentional alloying elements from unsorted scrap and the impact on mechanical performance is based on data mining from thermodynamic databases as well as from atom probe tomography. For the latter, a largely automatized workflow for detailed precipitate analysis was established (A. Saxena) – and immediately found applicable to entirely different material classes (Fig. 6).

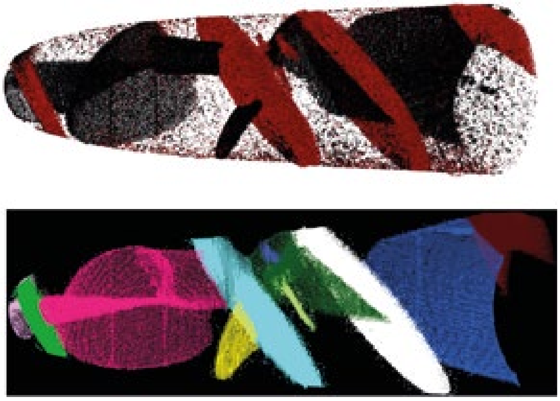

Fig. 6: *Automatic identification of precipitate phases via clustering in compositional space (upper image: black, red) in an APT data set from Fe-doped SmCo magnets, and subsequent segmentation into individual precipitates via DB-SCAN. APT data from N. Polin (MA).*

Thermodynamics and Kinetics of Defects (L. Huber)

The "Thermodynamics and Kinetics of Defects (TKD)" group headed by L. Huber since 2019 focuses on the behaviour of defects -- grain and phase boundaries, dislocations, and point-defects at the atomic scale using classical, quantum, and machine learned representations. An example of this work, a defect phase diagram, is shown in Fig. 7. Since its inception, the group has had two MSc students graduate: R. Dsouza studying the impacts of anharmonicity on diffusion ("Fully anharmonic self-diffusion coefficients using the Finite Temperature String method", RWTH Aachen, Dec. 2020), and V. Bhuva studying atomic clustering behaviour ("Algorithms for optimal chemical ordering ", Universität Passau, Sept. 2021). R. Dsouza has continued in the group pursuing his doctorate with a focus on anharmonic contributions to free energies. In Feb. 2020 M. Poul also joined the group as a PhD student. His work lies within our collaborative research centre CRC1394 with RWTH Aachen (see p. 76) and is on developing machine learned potentials suitable for complex phases and solute-defect interactions. The scope of research activities within the TKD group is given more completely on page (see p. 41).

Members of the TKD group are also heavily involved in the development of the CM department's open-source pyiron IDE (see p. 72). In September 2020 the group hired N. Siemer as a full time software developer. As part of his work to bring pyiron beyond atomistic simulation and make it relevant for our experimentalists, he has worked on a graphical user interface (GUI) for pyiron and collaborated with our experimentalist colleagues to develop comprehensive metadata schemes for digitalizing over 22 different experimental activities, e.g. TEM measurements, tensile tests, and various sample preparation routines. L. Huber and N. Siemer, together with M. Poul, were also heavily involved in the evolution of pyiron from a single monolithic package to a collection of modules, each with its own specialization and all with state-of-the-art continuous integration/continuous development (CI/CD) workflows. Since this split the TKD group has contributed to various specialized modules, e.g. incorporating finite element codes to bring pyiron into the regime of continuum mechanics (L. Huber), and powerful streamlining for the architecture pyiron uses for data storage and retrieval (M. Poul). R. Dsouza and V. Bhuva's scientific work is also fully integrated with the pyiron environment. In particular, R. Dsouza along with L. Huber and a collaborator at Montan Universität Leoben developed a generic scheme for workflows on directed cyclic graphs.

In addition to digital infrastructure, TKD members are involved in a variety of organizational and social infrastructure activities. R. Dsouza and M. Poul represent the CM department to MPIE's PhD student board, and L. Huber serves on the research data management team for CRC1394 and MPIE TeamGreen (see p. 103). M. Poul has also been particularly active in workshop organization, helping to coordinate and execute both the RUB ICAMS POTENTIAL workshop [85] and a pyiron workshop on calculating phase diagrams [86]. M. Poul and R. Dsouza also acted as teaching assistants in J. Neugebauer's recurring electronic structure course and L. Huber facilitated a series of hands-on simulation sessions for a graduate level course at RWTH Aachen in the winter semester of 2020/21.

Microstructure and Mechanics (E. Bitzek)

The new group of E. Bitzek (see p. 37) on "Microstructure and mechanics" ideally complements the expertise already present at CM and strengthens the departments activities regarding mechanical properties and failure of materials. With its background and its methods, the new group can directly contribute to research throughout the departments, as has been already demonstrated by several collaborations. Collaborations with groups working on high entropy alloys and concentrated solid solutions, high temperature materials, hydrogen in materials, nanomechanics and nanostructured materials are expected to lead to synergies with the microstructure and mechanics group. Additionally, the new group broadens the scope of MPIE by including new classes of materials like bulk oxide, polymer or metallic glasses, and strengthens its activities in research data management and the NFDI initiative.

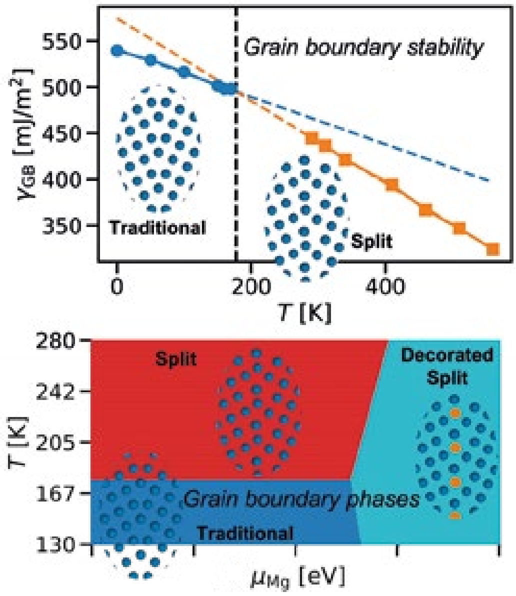

Fig. 7: *Top: A grain boundary phase transition in Al by classical molecular statics. Bottom: An simplified defect phase diagram for the same boundary in an Al-Mg alloy as function of temperature and Mg chemical potential.*

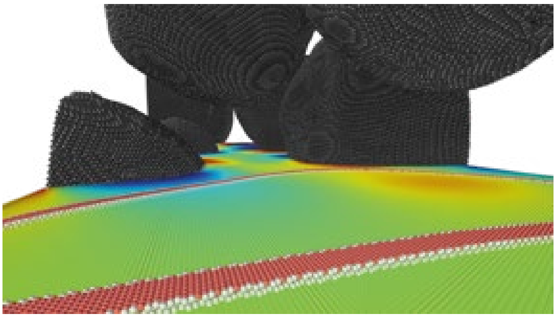

Fig. 8: *Superdislocation interacting with precipitates obtained by APT of a superalloy. The colour represents the resolved shear stress acting on the superdislocation caused by the lattice misfit of the precipitates, which can affect the strengthening mechanism by decoupling the superpartial dislocations [87].*

Electrochemistry and Corrosion (M. Todorova)

The “Electrochemistry and Corrosion” group aims at understanding how interactions with the environment affect and modify materials and their properties. Hereby, the strong focus on corrosion and electrochemical processes, where solid/liquid interfaces play a central role, continuously challenges the use of conventional techniques and drives us to extend existing methods and/or develop new approaches, enabling us to gain an in-depth atomistic understanding of the physical and chemical processes taking place at surfaces and interfaces (Fig.9). Particularly fruitful in this context was the close collaboration with the groups of S. Wippermann (GO) and C. Freysoldt (CM) leading to the development of a novel thermopotentiostat scheme (see p. 69), which allows for a realistic description of electrified solid/liquid interfaces [15].

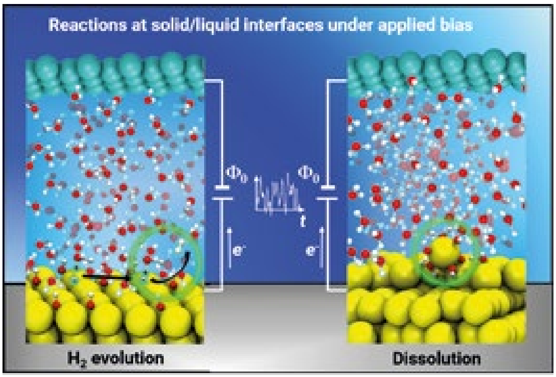

Fig. 9: *Reactions at solid/liquid interfaces under realistic conditions of applied bias. The voltage is applied between two electrodes (yellow and cyan balls), which sandwich the water electrolyte (oxygen: red, hydrogen: white). Calculated reactions and reaction paths occurring at the interface are highlighted. Left: H_2 evolution on Pt(111). Right: Mg dissolution under anodic conditions.*

Exploring the connection between applied potential and water interactions with solid surfaces the work of S. Surendralal [16] provided fascinating insights into the $H/H_2O/Pt(111)$ system und led us to re-evaluate existing models of water-metal bonding, Fig. 10 (see p. 224). We continue with this work by evaluating the energetics of the system, investigating both free energy profiles gained from the performed ab initio molecular dynamics calculations, as well as the impact a change in the hydrogen chemical potential has on the H coverage at the surface. Recently, the work was extended to the consideration of a more open surface orientation Pt(100) by Z. Wang. In both cases, we closely collaborate with the group of Prof. R. K. Campen (University Duisburg-Essen) exploring spectroscopic signatures to gain a better understanding of mobility and reactivity at and of the surface.

The award of a FP-RESOMUS fellowship (see p. 86) to Z. Wang enables him to address very fundamental questions related to charge transfer reactions, which are at the heart of any electrochemical process, at solid/liquid interfaces. Using model systems, he explores, for example, the interaction between solvation shells or the change in water screening properties during a dissolution process.

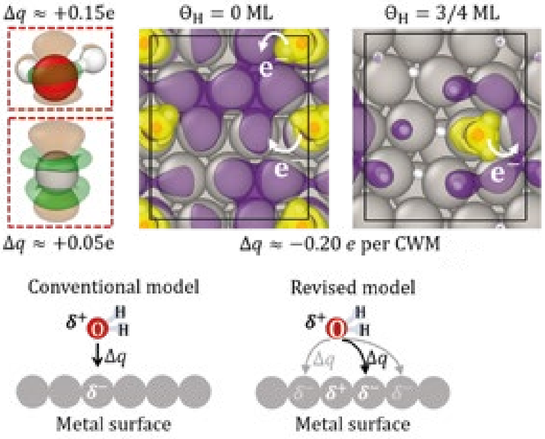

Fig. 10: *Top: Charge density difference showing the charge redistribution in the $H/Pt(111)/H_2O$ system. Side view of the charge distribution of a water molecule chemisorbed on top of a Pt atom with respective charges Dq obtained by integration over the volumes indicated by the red dashed lines (left). Top view of the charge redistribution for different coverages of co-adsorbed H (middle, right). Bottom: Conventional model for chemisorbed water-metal bonding (left) and revised model, based on our findings (right). Adapted from [16].*

Further work concerned with the transfer of electrons in the context of electrochemical reactions was carried out in collaboration with the group of D. Marx (Ruhr-Universität Bochum) within the Cluster of Excellence RESOLV. S.Yoo utilised alignment techniques commonly used in semiconductor physics, to identify the mutual position of relevant energy levels with respect to each other. This allowed elucidating the role of electron transfer between a surface oxygen vacancy on TiO_2 and an adsorbed Au nano-cluster, highlighting the importance of considering the dynamic nature of the cluster and providing fascinating insights into the catalytic activity and reactivity of this system [17].

During our investigations related to the role of point defects in the growth of oxide barrier layers during corrosion, we realised that materials like ZnO, important in the context of the corrosion protection of steels, suffer some limitations in the description of their electronic structure. S. Yoo tracked this back to the presence of spontaneous polarizations, which is not accounted for by conventional passivation schemes used when modelling semiconductor surfaces. This led us to develop in collaboration with Prof. C. Van de Walle (UCSB, USA) a robust generalized passivation method that accounts for the effect of spontaneous polarization for pyroelectric materials and correctly describes the asymptotic bulk limit [46].

While ab initio techniques are a prerequisite to obtain an accurate description of the electronic structure during processes triggered by interactions with the environment, they impose restrictions like, e.g., system size or achievable time scales. Aiming to overcome these and other limitations, and further improve the realism of our models in describing processes at electrified solid/liquid interfaces, we closely collaborate with the group of S. Wippermann (GO). During weekly hackathon sessions we explore various ideas and directions aiming to overcome such limitations, and/or explore new directions.

The use of thermodynamic concepts and various flavours of defect phase diagrams have always been an integral part of the activities in the "Electrochemistry and Corrosion"group. The establishment of the CRC1394 (see p. 76) has recently intensified these activities, which are carried out in close collaboration with the groups of C. Scheu (SN), T. Hickel (CM) and L. Huber (CM). S.K. Kanachari Bavajigari focuses on the solid solution of Ca and Al in a Mg matrix. Constructing surface and interface Pourbaix diagrams, i.e. thermodynamic diagrams providing information about the stability of phases depending on the electrode potential U and the pH of the solution, he explores the connection to the chemical potential variations of the involved species. His recently obtained Alexander von Humboldt postdoctoral fellowship will allow him to explore the atomistic mechanism of the role of Fe in Mg corrosion. E.I. Saad, who looks into routes for efficient free energy calculations, supports these activities.

Thermodynamic modelling and surface phase diagrams have also proven extremely valuable during the course of recent collaborations with the group of B. Gault (MA). They enabled us to explain the role of H as a contaminant in Atom probe experiments [59] (see p. 198) or account for different conditions employed to synthesise Pd nanoparticles. In close collaboration with the groups of B. Gault (MA), T. Hickel (CM), C. Scheu (SN) and O. Kasian (GO) we were able to gain amazing insights into the contamination of nanoparticles during synthesis [18] and its impact on the catalytic activity of such particles (see p. 198 & 184).

Growth Modelling project group (L. Lymperakis)

The growth modelling project group focuses on the epitaxial growth and the properties of semiconductors, nanostructures, and 2D heterostructures by means of ab-initio based simulations. Within the reporting period L. Lymperakis is Co-PI of an EU and BMBF co-funded project (UltimateGaN: Research for GaN technologies, devices and applications to address the challenges of the future GaN roadmap) and a DAAD (Deutscher Akademischer Austauschdienst) funded project (Strain Tuning of III-V Semiconductor Nanowires, TUNE). Topics addressed by the growth modelling group include, but are not limited to surfaces and extended defects in materials for power- and opto- electronic applications, synthesis and properties of novel III-Nitride ternary alloys, and interfaces in Silicon.

Group III-Nitrides constitute one of the most important families of semiconductor materials with technological applications in the fields of energy efficient optoelectronic and power electronic applications. Crystal defects, in particular dislocations constitute a long-standing controversial topic in these materials. Although highly efficient optoelectronic devices operate at dislocation densities as high as 10^8 to 10^{10} cm^{-2}, GaN-based power electronics, a key component in future smart grid power applications, is severely affected by them. Dislocation and associated V-pits, i.e., structural defects which are formed when dislocations pin a surface or an interface, have been proposed to be the root cause of device leakage and breakdown and are considered to be one of the major limiting factors in achieving the full potential of nitride-based power electronic devices. An intriguing feature of these defects is that experimental evidences suggest that they are associated with open core structures, thus forming nanopipes with diameters of a few nms.

The formation of both nanopipes and V-pits is the result of a complex interplay between strain energy and surface energies. A necessary prerequisite to control the formation and the properties of these defects is to derive the surface energies of low index semipolar and nonpolar planes with respect to the energy of the (0001) GaN surfaces. In a first step, S. Yoo developed a novel reconstruction inspired passivation scheme that allows to unambiguously investigate the energetics and electronic properties of semipolar surfaces of semiconductors with a singular polar axis [52]. This scheme is generic and robust and can be straightforwardly employed in first principles investigations of low-symmetry surfaces as well as in high-throughput and/or machine learning studies. Based on this scheme S. Yoo calculated the surface energies of low index GaN planes and constructed a Wulff diagram as well as a 'V-pit' phase diagram, which describes the equilibrium size and shape of V-pits as a function of the ambient growth conditions. This diagram reveals that under typical growth conditions, the GaN polar planes are intrinsically unstable against the formation of V-pits with equilibrium lateral sizes up to a few tenths of a nm at sites where screw threading dislocations reach the surface. The defect formation is driven by the preferential decoration of the surfaces by hydrogen, which reduces the surface energies.

The formation and the properties of dislocation induced nanopipes in III-nitrides was investigated by combining first principles with large scale empirical potential calculations (see p. 190). Based on these calculations we constructed a dislocations' phase diagram which describes the energetically most favorable core structures as function of the growth conditions. A general trend that emerges from the aforementioned phase diagram is that nanopipes are energetically favorable under technologically relevant growth conditions. Although nanopipes exhibit large free surface areas which increase the energy, they can be energetically favorable if the surface energy is compensated by the core and strain energy of the material removed to create the open core dislocation. Under the aforementioned conditions the cation and anion dangling bonds at the open core inner surfaces are passivated by NH_x molecules and H atoms, respectively. This reduces considerably the surface energy and the formation of nanopipes with hexagonal cross section and equilibrium diameters ranging for ≈1 to ≈2 nm is energetically favorable. The formation of nanopipes has important implications for the efficiency and reliability of power electronic devices: Nanopipes and the associated inner surfaces constitute efficient paths for impurities diffusion and offer high density of active sites for incorporation.

Using its strong expertise in ab initio techniques and compound semiconductors, the group was instrumental in performing a wide range of joint computational and experimental studies. Examples are studying the optoelectronic properties and carrier confinement in InGaN quantum structures [66], strain engineering to achieve high In content InGaN Quantum Wells [67] (in collaboration with the Leibniz Institute for Crystal Growth, Berlin), the substitutional synthesis of sub-nanometer InGaN/GaN quantum wells [68] (in collaboration with the Aristotle University of Thessaloniki, Greece and the Helmholtz-Zentrum Dresden-Rossendorf, Dresden), the investigation and design of novel $Al_{5+\alpha}Si_{5+\delta}N_{12}$ compounds [69] (in collaboration with the Université Côte d'Azur, CRHEA-CNRS, France), or unravelling the mechanism leading to semi-insulating Carbon doped GaN [70] (in collaboration with Infineon Technologies Austria).

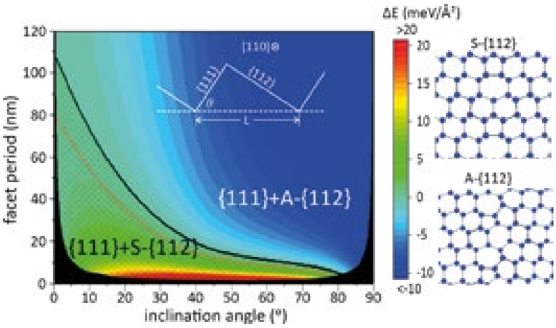

Fig 11: *Interface phase diagram showing the most stable interface reconstructions and orientation (faceting) as function of the GB inclination angle in silicon. The solid black curve indicates the boundary between GBs having an asymmetric (A) - or symmetric (S)-{112} facet. The cross-hatched area denotes the stability region of the higher energy S-{112} facets. The black shaded area marks the region of geometrically inaccessible facet periods and inclination angles. Inset: Schematic representation of a Σ3 tilt GB (dashed line) inclined with respect to {111} faceted toward {111} and {112} facets. Right panel: Relaxed atomic geometry of the S-{112} and the A-{112} GB viewed along ⟨110⟩. Adapted from [21]*

Applying its deep expertise on surfaces the group extended its activities in the investigations of interfaces in polycrystalline materials. In multi- and polycrystalline Si, the base material in today's photovoltaic industry, grain boundaries (GB) severely impact device performance. GB faceting severely impacts their behaviour. The mechanisms underlying faceting of GBs in Si were investigated by employing DFT and MEAM (Modified Embedded Atom Method) potential calculations [21]. The picture deduced by our calculations contradicts the common perception that the properties of faceting are merely driven by the anisotropic GB energies. Although anisotropic GB energies are a prerequisite for GB faceting, higher energy metastable GB phases are stabilized by thermodynamics and not kinetics when constituting the facets at line junctions (Fig 11). This insight has implications for the design of electronic and structural materials: Microstructures that allow for large facet periods stabilize line junctions accommodated by dislocations. In contrast, fine granular structures that limit facet periods promote line junctions without extended line defects and long-range strain fields.

Complex Concentrated Alloys (CCA) project group (F. Körmann)

The "Complex Concentrated Alloys (CCA)" research group of Fritz Körmann, established back in 2018 (see p. 55), aims in particular at the method development and application to complex concentrated alloys [8] including the prominent class of high entropy alloys (see p. 210, p. 194, p. 208).

Machine learning potentials – method development

A key achievement within the last years has been the combination of modern machine learning interatomic potentials (MLIPS) with ab initio calculations [1-4]. Two kinds of MLIPS have been applied to the challenging class of multicomponent alloys. One is the low rank potentials [1, 3, 4], a highly efficient on-lattice potential, suitable to explore, in combination with Monte Carlo simulations chemical orderdisorder transitions in multi-component alloys [1, 3, 4]. It can account for local lattice relaxations, which can qualitatively alter the computationally predicted ordered phases [1]. Short-range order, which impact on materials properties is currently attracting significant attention, can be readily computed. Applications include prototypical bcc NbMoTaW and AlNbTiV alloys [1,4] as well as recently discovered [73] ultra-strong fcc VCoNi alloys [3].

The second type of MLIPS are the moment tensor potentials (MTPs), fitting accurately energies, forces and stresses. Based on thermodynamic integration, highly accurate free energies, including anharmonic contributions can now be computed for multicomponent alloys, outperforming previous empirical potentials [2]. In combination with active learning [41] and novel structural descriptors [74], these potentials can be used to explore wide composition and temperature ranges to predict temperature-compositional phase diagrams such as the omega-bcc-liquid stability in bcc TiZrHfTa alloys [41].

Selected applications

The vast compositional phase space and chemical complexity of multicomponent alloys offers possibilities to

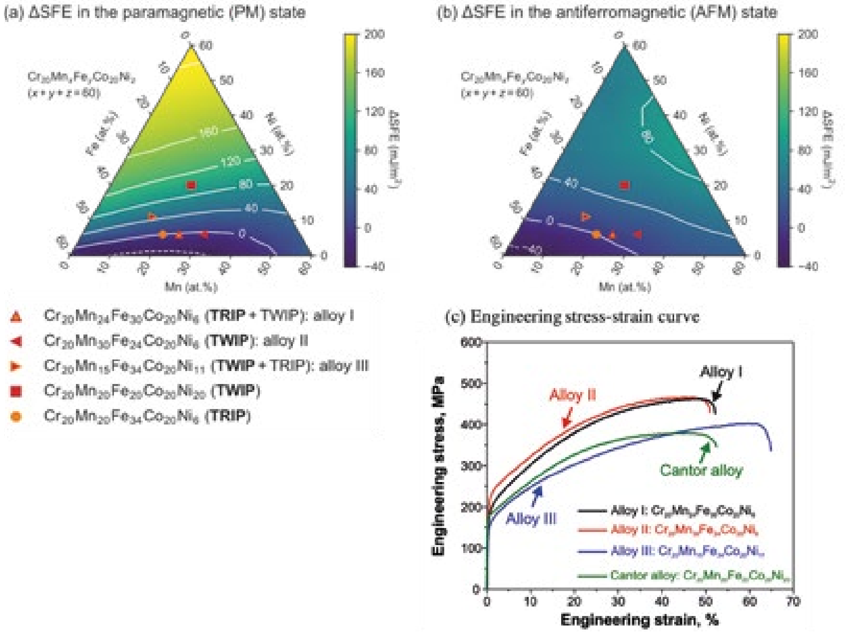

Fig. 12: *(a), (b) Difference in the Stacking Fault Energies (SFEs) of quinary $Cr_{20}Mn_xFe_yCo_{20}Ni_z$ CCAs compared to a reference alloy $Cr_{20}Mn_{20}Fe_{34}Co_{20}Ni_6$ in the (a) paramagnetic and in the (b) antiferromagnetic states obtained from ab initio calculations [75]. Triangle symbols show the experimentally investigated compositions. Two reference alloys, namely, the Cantor alloy (square) and $Cr_{20}Mn_{20}Fe_{34}Co_{20}Ni_6$ (circle), which is known to show transformation induced plasticity (TRIP), are also shown. The colors of the symbols show the dominant deformation behavior of the corresponding compositions; orange and red are for TRIP and twinning induced plasticity (TWIP), respectively. (c) Comparison of mechanical responses of three investigated alloys with Cantor alloy.*

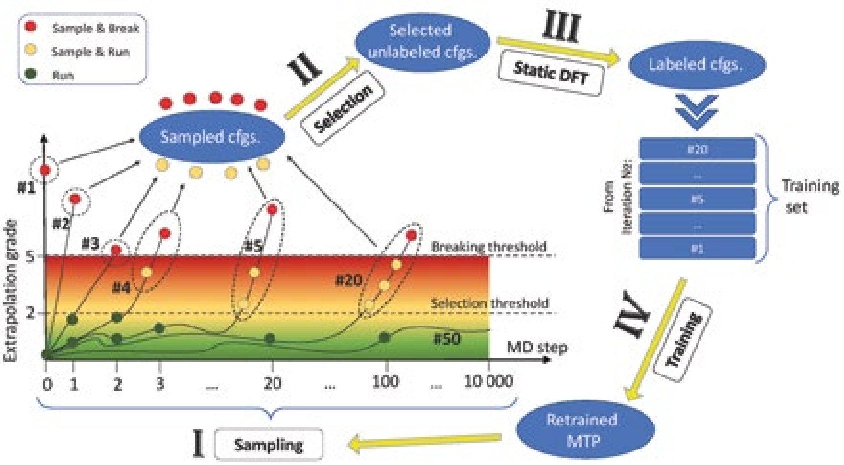

Fig. 13: *Graphical representation of the active learning schema used to design Machine Learning Moment Tensor Potentials for bcc multicomponent alloys [41]. (I) Configurations (cfgs.) are sampled from MD trajectories (II) Sampled configurations are shortlisted based on the MaxVol criterion [41]. (III) After assigning DFT energies/forces/ stresses they are appended to the training set. (IV) Training of a new MTP able to "work" in larger configurational space. This procedure is repeated until no new configurations are sampled from the MD trajectory.*

tune alloy composition for improving intrinsic materials properties. Key ingredients in this respect are, e.g., local lattice distortions and atomic level pressures [7, 10 ,12] as well as stacking fault energies [75, 79, 80] (see p. 194 & p. 208). Based on high-throughput calculations and careful consideration of magnetic effects, the intrinsic interplay of magnetic entropy and chemical composition has been revealed for Cantor based fcc alloys, allowing to develop in cooperation with our experimental colleagues a number of new transformation and twinning induced plasticity high entropy alloys [75]. Interstitial alloying introduces a further challenge due to the immense phase space of local chemical environments. New thermodynamic statistical methods were developed to account for this allowing to predict the impact of interstitial elements for fine-tuning the alloys stacking fault energies [5, 13, 81]. Further opportunities are in the field of precipitation-strengthened CCAs [14, 82]. To improve the magnetic properties tuning with non-magnetic elements [82] as well as spinodal composition has been introduced as design concepts for CCAs [76] showing that in combination with ab initio predicted energetics, the magnetic properties such as Curie temperature and saturation magnetization can be readily improved (see p. 210). Also surface stability of CCAs has attracted enormous attention recently as potential game changers in heterogeneous catalysis, showing much higher catalytic activities as simple rule of mixture would suggest. Recent research efforts are therefore also devoted to study surface segregation and stability of various CCAs [22, 9].

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Department of Interface Chemistry and Surface Engineering (GO)

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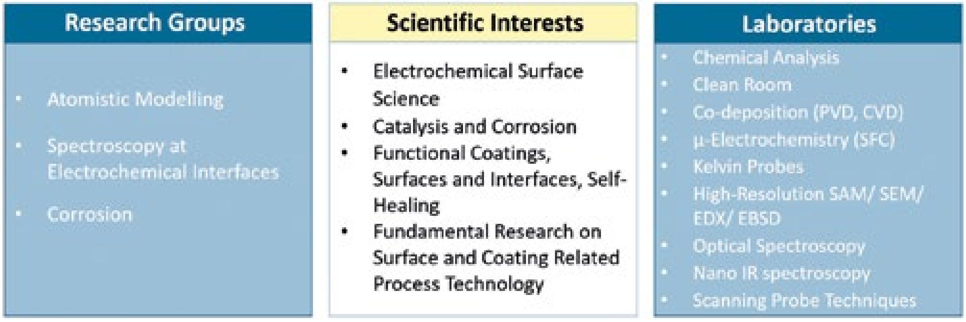
Introduction

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 as structural (in particular steels and other alloys) and functional materials, e.g. for fuel cell catalysts, pre-treatments and smart coatings amongst others. The department currently hosts four 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.

Of crucial importance in the last three years was to stabilize the department. Since the head of the department M. Stratmann, took over as president of the Max Planck Society in June 2014 and is officially on leave from his position at the MPIE, significant changes took place in the department. M. Rohwerder took over the coordination of the department and J. Neugebauer (head of the department "Computational Materials Design") acts as temporary head of the department. Most notably the number of research groups shrank quickly from six in 2014 to two in 2019. However, the research group of A. Erbe (Optical Spectroscopy) remained very active as a guest group until end of 2019, and the one of K. Mayrhofer (Electrocatalysis) too, to be followed by the very active guest group of O. Kasian (Dynamic Electrocatalytic Interfaces, until end of 2021). In 2020 the early career research group "Spectroscopy at Electrochemical Interfaces" was established in the GO department as joint research group of the MPIE and the cluster of excellence RESOLV (www.solvation.de) located at the Ruhr-Universität Bochum (RUB). The group uses interface spectroscopic methods to study solvation and other dynamic effects on solid surfaces interfaces (see p. 45). By establishing this new group important expertise could be regained.

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), which is centred at the RUB's 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 (see p. 86).

With its versatile experimental and theoretical expertise (Fig. 1) the GO department is in the unique position to assist and promote also diverse **industrial research especially in investigating the underlying fundamental electrochemical reaction mechanisms and kinetics**.



Research Groups

- Atomistic Modelling
- Spectroscopy at Electrochemical Interfaces
- Corrosion

Scientific Interests

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

Laboratories

- Chemical Analysis
- Clean Room
- Co-deposition (PVD, CVD)
- µ-Electrochemistry (SFC)
- Kelvin Probes
- High-Resolution SAM/ SEM/ EDX/ EBSD
- Optical Spectroscopy
- Nano IR spectroscopy
- Scanning Probe Techniques

Fig. 1: *Current research portfolio and expertise.*

For instance, the 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. 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 (see e.g. "Electrocatalysis" and "Spectroscopy at Electrochemical Interfaces" reports below). The knowledge obtained in the fundamental research on electrochemical key reactions such as oxygen reduction and oxygen evolution play a crucial role in helping us to unravel practical problems met in industrial applications or processes such as in corrosion, batteries and fuel cells.

Fig. 2: *Part of the GO department with M. Stratman during an excursion at the department retreat at Ringberg Castle in 2021.*

Several research projects focus on industrial processes such as pickling and 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 department 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 even through zinc-based alloy coatings.

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. Comparison with experimental results, however, is difficult, because reliable experimental *in situ* data for instance of reaction products are difficult to obtain from the electrochemical double layer region, which is buried from most surface analytical techniques by a layer of bulk electrolyte. Thus, experimental feedback is more or less missing. Of increasing importance here is our surface science approach for fundamental investigation of electrode surfaces. This is a long-term research topic within the department. 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. 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, as for instance surface analytical tools such as near ambient pressure x-ray photoelectron spectroscopy (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. However, most of this work so far has been carried out on palladium terminated surfaces. Hence, besides investigating ORR on such electrodes, also very fundamental research on the general applicability of the "electrode in the dry" concept on different electrode materials, such as Pt, Ir and Au, is carried out (see "Corrosion" group report below).

This experimental part of our activities on electrochemical sciences is accompanied by work in the atomistic modelling group where in cooperation with the CM department a novel approach to control the electrode potential was developed, that can be used equally well to perform empirical or *ab initio* molecular dynamics simulations (see "Atomistic Modelling" group report).

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. One example is the "electrodes in the dry", but the main activities are carried out in the MPIE-RUB early career research group "Spectroscopy at Electrochemical Interfaces" (see below and p. 45).

Corrosion

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

During the last three years the corrosion research of the department covered a wide range of topics in the areas of aqueous and atmospheric corrosion processes and their inhibition, covering both fundamental and applied aspects. A key technique for corrosion research remains 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 department, has become a routine technique for corrosion research and was applied on a wide range of materials, also in the last three years.

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. However, it was now found that there are also exceptions from this (see "Corrosion" group report). Concerning atmospheric corrosion, our main focus is on the delamination of organic coatings. Organic coatings are commonly employed to protect materials 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 pre-treatments 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 department 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. In the reporting period important insights were obtained on the fundamental mechanisms of this process (see p. 85 and below).

High temperature reactions

Reactions at high temperatures is another topic that is investigated within the GO department. Special focus has been on 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, where they cause significant external and internal oxidation. These relatively short processing steps are generally not much investigated yet and are determined by kinetics of oxygen uptake, nucleation and growth of oxides and only to limited extent by diffusion, usually considered of key importance in high temperature oxidation, which leads to final morphologies that are often far from equilibrium. More recently this research is replaced by investigations on direct reduction of iron ores by hydrogen (see "Corrosion" group report).

Functional surfaces, interfaces, coatings and materials

Our research on functional surfaces, interfaces and coatings is mainly focused on improving the long-term stability of coatings applied on metallic substrates. The targeted main functionalities of coatings and interfaces are smart sensing of and protection against corrosion. For this, new concepts are developed and in-depth investigation of crucial fundamental processes were performed. Of especial importance for achieving high-performing self-healing response are fast trigger signal spreading and also sufficiently high transport of active agents from within the coating to the defect site. This requires an in-depth fundamental understanding of these processes and about the possibilities to optimize them. The related research covers the whole coating system, from nano-containers for storage of active agents, over suitable active agents to tailoring properties of all involved surfaces and interfaces. Especially promising for optimized trigger signal spreading and transport of active agents seem to be interfacial layers of conducting polymer (see “Corrosion” group report).

Also, bulk functional materials are investigated, such as e.g. quantum dot solids which are of high interest for creating novel quantum materials with targeted properties with possible applications, e.g., as next-generation light absorbers for photovoltaics, photoelectrochemistry and power electronics. III-V semiconductor-based Quantum dot solids, consisting of e.g. InP or InGaP nanocrystals, are among the most widely investigated materials systems due to their potentially superior optical properties and lower toxicity, compared to commercially available II-VI quantum dot solids. Whereas narrow emission line widths are readily achieved in II-VI quantum dot solids, III-V systems still suffer from inferior colour purity due to broad emissivity and poor photoluminescence quantum yields. We recently demonstrated that nanocrystal stoichiometry dispersion is a major source of trap states and largely responsible for the observed emission broadening (see “Atomistic Modelling” group report).

Another important topic are electro responsive ‘smart’ interfaces which are of interest for applications in microfluidics, separation systems, biosensors and -analytics. (see “Spectroscopy at Electrochemical Interface” group report).

Industrial processes

The expertise of the department is of great relevance for the investigation of fundamental aspects of industrial processes.

Fundamental problems of oxidation and hydrogen uptake during industrial production steps of high strength steel sheet have been a longstanding focus of the department and many of the activities within the reporting period on these topics are based on that earlier work. A high performing high temperature lab is available for fundamental investigations of according industrial processes, which is currently restructured in order to support the new inter-departmental focus on direct iron ore reduction.

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 the role of surface treatments on the interface chemistry on cold welding of steels and aluminium alloys was investigated (see below reports by the “Corrosion” group and the former “Interface spectroscopy” group). The department was here mainly involved with chemical and electrochemical surface treatment and *ex situ* investigation of the resulting interface.

Scientific Groups

Corrosion (M. Rohwerder)

The main scope of this group is to address fundamental questions of corrosion and surface and coating technology by isolating the crucial problems behind them and designing model experiments and model samples for their systematic investigation. Three exemplary research projects, in collaboration with external partners, that stand quite nicely for the research in the group are: “H2 free - Investigation and modelling of hydrogen effusion in electrochemically plated ultra-high-strength-steels used for landing gear structures” within the CleanSky programme of the Horizon 2020 - Research and Innovation Framework Programme; ”MAXCoat - MAX-Phase coatings for corrosion protection of bipolar plates for mobile fuel cells”, financed by the Federal Ministry for Economy and Energy; and “PredictCorr - Prediction of durability and lifetime of organic coated metals under long-term environmental conditions”, financed by the Flamish Research Foundation (see p. 85).

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, as could now be shown even for the case that the exit side is not immersed into electrolyte [1], just as it is of relevance for the situation met during corrosion driven delamination under atmospheric condition.

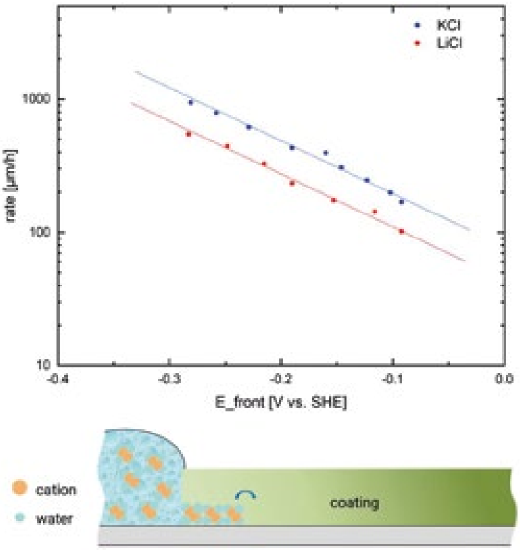


Fig. 3: *Top: delamination rates measured for a PVB (polyvinlybutyral) coating applied onto iron, for either KCL or LiCl as electrolyte in the defect, plotted as a function of the potential at the delamination front. Since the rate also depends on cation size, oxygen reduction seems not the rate determining step here. It is assumed that rather the insertion of cations into the yet intact interface (bottom) is the rate determining step.*

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 [2-4], which are considered for developing dedicated model samples for very fundamental studies. The other set is currently more important and is focussed on technically more relevant samples, such as coated iron/steel and zinc, and some experiments were also performed on coated aluminium alloy. In the reporting period the main focus was on coated iron and steel, mainly within the PredictCorr project (see p.85). The idea of that project is to provide the tools for a long-term prediction of coating performance. At the MPIE the focus is on unravelling the underlying mechanisms and providing information about the corresponding kinetics. One planned activity is to investigate the oxygen reduction kinetics at the buried interface between metal and organic coatings, using the hydrogen permeation based method developed in the group [1]. To be precise, the investigations should include the interface at different stages of the delamination process: the intact interface, where degradation is initiated right at the delamination front, in the delaminating area, where there will be furthermore different stages of delamination, depending on the exact position, and within the delaminated area. Hence, owing to the complexity of this task it was decided to focus first on the very first step of delamination, i.e. is the insertion of cations, migrating from the defect site, into the intact interface. This leads to a correlated decrease in potential at the interface and thus enabling the onset of oxygen reduction. Hence, this can be considered as the first step of delamination. So far, the role of cations in cathodic delamination was solely discussed as migration of cations from the corroding defect to the intact interface, i.e. along the delaminated interface. This cation migration is required to ensure charge neutrality, i.e. to compensate the electron flow along the interface from the defect to the delaminating and delaminated interface, that is required for the oxygen reduction reaction at the decreased potentials. It was assumed until now, based on the work by M. Stratmann et al. that a square root dependence on time for the overall delamination rate is associated with cation migration as a rate determining step. A linear time dependence, on the other hand, is generally believed to be indicative for oxygen reduction as rate determining step. However, as mentioned, the very first step has to be that cations move into the intact interface, which, if rate determining, is expected to also possibly lead to a constant delamination rate. The idea for investigating this in more detail was at first to perform studies in the absence of oxygen, such as e.g. in humid nitrogen. In that case no oxygen reduction occurs and hence no delamination, i.e. the interface stays undamaged. It was already shown by M. Stratmann et al. that in that case the ingress of cations into the intact coating can be monitored by Scanning Kelvin Probe (SKP). It seems reasonable to assume that the overall rate of this cation ingress is determined either by the migration of cations along this interface or by the first insertion of cations in the yet cation free interface at the migration front. Within the PredictCorr project different model samples, featuring different coating types and different surface treatments of the underlying steel were provided and it was found that for most of these the overall rate was depending on the square root of time and that the initial migration behaviour in nitrogen atmosphere was nearly identical to the one of delamination. This is difficult to explain, if cation migration was the rate determining step of delamination, as in the one case the cations migrate along a delaminated interface, in the other case along an undamaged, intact one (see p. 85). Hence, it seems likely that the rate determining step in both cases might be the initial ingress of cations into the yet unaffected interface, also denominated in the group as cation insertion. Also, other indications for this were discovered in other research projects. For instance, it was found that adsorbed species such as CO_2 [5] on coated zinc and even O_2 on novel chromium coatings [6] have a huge effect on delamination/migration. Since during delamination the delaminated interface is characterized by relatively high rates of oxygen reduction and for the case e.g. of zinc also by anodic zinc oxidation and dissolution, it seems unlikely that the presence of small amounts of CO_2 could have a significant effect on ion mobility at that interface. This means that the observed effects are most likely rather related to the intact interface, i.e. the initial cation insertion step into the intact interface.

Related observations were made within PredictCorr, too. For instance, the observed initial similarity between delamination behaviour in air and migration behaviour in nitrogen was found to change after a while (see p. 85).

For some of the coating systems the migration in nitrogen atmosphere slowed down after a few hours and in some cases even came to a total halt. It is assumed that this is due to changes at the interface caused by the change of atmosphere and is object of intense current research. Despite of the unexpected high complexity also of the cation insertion and migration processes, it was possible to make significant progress. Key to this was a new experimental procedure wherein the defect edge, where the delamination is initiated, is not left to freely corrode, but instead is stepwise polarized to a sequence of well controlled potentials. Thus, it was found that the cation insertion process at the delamination front depends sensitively on electrode potential at the front, but also on cation size (Fig.3). This is object of intense current research.

2. Intelligent self-healing concepts for corrosion protection

In the last three years the research on intelligent self-healing concepts for corrosion protection could build on many years of intense activities on that topic. While in prior works especially safe storage of active agents and their corrosion triggered release from capsules were at the focus of our research, as well as the functionality of intrinsically conductive polymers (ICP) as switchable encapsulation material and for use as isolated agglomerates for reducing delamination rate by surrounding protection zone effects [7, 8], the focus of the activities has now shifted towards additional coating functionalities, such as corrosion sensing and signalling within coatings [9], as well as combinations [10] , or improving the transport of active agents for corrosion inhibiting and/or restorage of damaged organic coating from their storage site inside a coating towards the defect. For the latter once more ICPs were investigated. While in the last reporting period it could be shown that ICP films can significantly enhance trigger signal spreading, thus ensuring a fast and widespread release of active agents upon onset of corrosion, now it was investigated in how far they also can enhance the transport of the released active agents towards the defect site. For this, a dedicated novel experimental set-up was designed and successfully utilized (Fig.4) and it could be shown that indeed especially for cationic and neutral active agents a significantly enhanced supply of these can be provided by large networks of (partially reduced) ICPs [11].

The reason for the excellent cation mobility in the partially reduced ICP network is that by electrochemical reduction ICPs are becoming at least to some extent cation-permselective. It is assumed that the also observed very high mobility of the uncharged active agents might be due to a correlated switch from rather hydrophobic to rather hydrophilic behaviour of the ICP upon (partial) reduction. This is object of current research.

Hence, in sum it seems that contrary to longstanding assumptions, based on our earlier findings, that large networks of ICP, such as continuous ICP films or extended agglomerates of ICP particles, would rather reduce the corrosion protection properties of a coating than improve it, when making use of these new functions, such extended networks might allow realizing novel smart corrosion protection coatings with significantly improved self-healing capabilities.

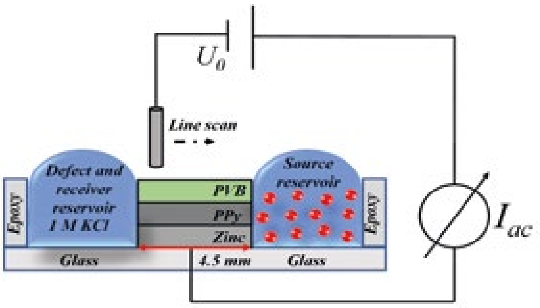


Fig. 4: *Schematic drawing of the set-up used for the transport studies: the coating system is placed between two reservoirs. One is for simulating the defect (left) and the other serves as reservoir for active agents. This allows to study the effect of variations in the coating system and of the nature of the different active agents on their transport through the bulk coating and alongside the different interfaces [11].*

However, for this it is important to ensure that the spreading of ICP reduction from a corroding defect site is at some point stopped, even if the corrosion in the defect cannot be stopped and continues. Otherwise, the coating would quickly fail over a large area. Now it was found that by use of suitable counter-anions, the reduction and delamination of continuous ICP layers cannot only be stopped after a certain while, but both can be reversed, i.e. a full self-healing of the ICP layer and restorage of the interface can be achieved. This is an important requirement also for full self-healing: the ICP film is quickly reduced and the interface delaminated for fast signal spreading, release and transport of active agents. But upon healing of the defect both ICP film as well as interface are restored again. Importantly, this occurs not only readily when the defect is successfully inhibited, but also without that, preventing disastrous failure of the coating. How that works even in the presence of a still actively corroding defect is, however, not fully understood yet, but object of intense current research. A new activity within the department is research on novel inhibitor concepts for mitigating delamination and corrosion, see e.g. [12].

3. Corrosion

While in the past the main corrosion activity within the department was mainly on organic coating delamination and the role of the metallic substrate (or rather the passive layer on its surface) beneath the organic coatings, in the last three years more classical corrosion topics have re-gained importance. Most notably passive layers and their failure are now of increasing research interest in the department, see e.g. [13, 14]. One main motivation for this is the search for novel materials for bipolar plates that are used in fuel cells. The challenge here is that on the one hand a highly passive surface layer is targeted, on the other hand at the same time a high conductivity. This is object of current research within the project MaxCoat (in cooperation with the Zentrum für Brennstoffzellentechnik in Duisburg and the Leibniz-Institut für Plasmaforschung und Technologie in Greifswald), where MAX phases, which are known to show high conductivity and high chemical stability, are investigated as a possible coating material for bipolar plates. Fast feedback on even smallest defects and the general electrochemical performance of these coatings is provided at the MPIE by means of the scanning flow cell method in combination with inductively coupled mass spectroscopy (SFC-ICPMS). This approach was also successfully applied in other projects, such as e.g. elucidating the corrosion protection performance of magnetron sputtered TiMgN hard coatings [15].

In fuel cells potential-triggered passivation of e.g. TiC supports may have a great potential for increasing lifetime of Pt-catalysts. Our results have shown that the deposition of a closed Pt film onto a TiC support protects the latter from dissolution up to about 1.05 VRHE. At higher potentials where Pt oxidation and dissolution occur, the underlying TiC heals out the defects and imperfections created in the Pt film by building up a protective oxide layer that stops further degradation [16].

Also, corrosion properties of novel light-weight materials are investigated. For instance, in cooperation with H. Springer from the MA department the effect of Al and Cr additions on the mechanical, physical and corrosion properties of Fe was investigated in a combinatorial approach for screening suitable compositions as the basis for the alloy design of novel lightweight corrosion resistant steels. It was found that upon decrease of Cr content in the alloy and increased Al content, also in the passive layer chromium is more or less replaced by aluminium while a quite significant degree of passivity is preserved [14].

On the other side of the spectrum of our activities on corrosion were studies on erosion-corrosion, with a focus on degradation processes as they occur in pipelines transporting slurries e.g. in the mining industry [17], and investigations on the effect of surface treatments on the stability and degradation of cold pressure welded components [18, 19].

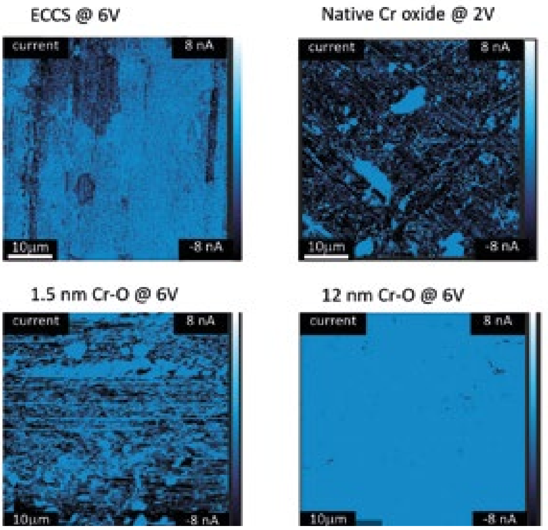


Fig. 5: *Current maps obtained by current sensing atomic force microscopy (CS-AFM) on differently terminated chromium layers (note the lower applied bias between tip and sample for the native chromium oxide covered sample). ECCS denotes the standard chromium coating deposited electrolytically from Cr(VI) containing electrolyte, which has to be replaced for environmental and safety reasons, and Cr-O, an electrochemically deposited additional chromium oxide film on top of a chromium layer deposited from trivalent Cr containing electrolyte (1.5 and 12 stand for 1.5 and 12 nm of the Cr-O film). The differences between the different samples are of interest as well as the heterogeneity.*

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 in significantly enhanced performance. In general, the composition, structure and the related properties of oxides are of utmost importance for the performance of coating systems applied on metals. In the reporting time an important activity was the investigation of the oxide layers on electrochemically deposited chromium coatings on steel, where strong differences in conductivity were found for different kinds of the terminating chromium oxide layers (Fig. 5).

Especially insulating was a strongly O-deficient metastable Cr-O phase [6], where already ultra-thin films showed only extremely low conductivity. Also, cathodic delamination was found to be strongly inhibited by such oxide films, which at the first look would be assumed to be directly linked to the low conductivity which would also suppress oxygen reduction.

However, it was also found that cation mobility on these oxides is also extremely low and interestingly depends on partial pressure of oxygen in the environment. By ambient pressure photo-electron spectroscopy (AP-XPS) it was found that indeed oxygen adsorption on these oxides is sensitively responding even on slight changes of oxygen partial pressure. This oxygen adsorption results in quite significant changes in potential upon switching between nitrogen and oxygen containing atmospheres, as can be measured by SKP. This has never been observed before for such delamination resistant samples. Usually a large response is a sign for fast delamination behaviour.

More recent is our research on the effect of hydrogen on the properties of the oxide in the passive layers of metals. Our motivation for this research is to investigate how the work function of different oxide, or rather the electrode potentials established on their surface in different environments, depends on hydrogen activity. This knowledge can be used e.g. for the study of oxygen reduction at buried interfaces, and for hydrogen detection in or measurement of its permeation through materials at high local resolution. This is closely related to our research on the "Electrochemistry in the "dry".

5. 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 on the (oxide covered) surface of a metal upon switching the atmosphere between air and nitrogen and back as an indicator for its reactivity. However, electrodes in the "dry" are of general importance. Many phenomena in corrosion and electrochemistry are occurring on electrodes that are not immersed into bulk electrolyte or covered by bulk-like electrolyte layers, and these are still not well understood. Maybe the most fascinating result of this work is that the electrochemical oxygen reduction reaction on the surface of palladium just covered by one to two monolayers of water, is in principle the same as on an electrode immersed in acidic bulk electrolyte, just without the mass transport limitation for oxygen [1]. Because for an electrode immersed in electrolyte the double layer is more extended, this directly raises questions about the structure of the electrochemical double layer, which is here confined to just one or two monolayers with protons as counter ions, and how this determines the reaction kinetics. This question is at the focus of intense research on emersed electrodes, where it is possible to include also other ions into the electrochemical double layer and to tune the water layer thickness via the relative humidity in the atmosphere the emersed electrode is exposed to. It could be shown that during emersion even into dry nitrogen atmosphere a water layer is preserved and that the water molecules in this layer are assuming an orientation that is determined by the potential. The effect of additional water layers, adjusted by higher relative humidity, is object of current research, as well as the question what their effect is on the kinetics of reactions such as oxygen reduction. While the investigations on emersed electrodes are so far mainly carried out for gold as electrode material, the "hydrogen electrode in the dry" concept is investigated in parallel for other materials besides palladium [1], such as iridium and gold. The idea is to combine the concept of the emersed electrode with the concept of polarisation from the backside by adjusting there a well-defined H activity [1], usually by electrochemical polarisation. Interestingly, the "hydrogen electrode in the dry" on Ir and Au is depending sensitively on relative humidity. While for Pd there is 1:1 relation between potential applied from the backside and potential measured by Kelvin Probe on the "dry" electrode in low as well as in high relative humidity, for Ir, for instance, such a 1:1 correlation is observed only at high humidity, while at lower humidity the response is less than 1:1, the closer to it the higher the humidity. This is object of current research. Interestingly, the linear relation remains. It should be pointed out here, that it still remains unclear why a linear relationship is observed in the first place, since as the equilibrium reaction on the electrode surface is: $H_{ab} \leftrightarrow H^{ad} \leftrightarrow H^{+}+e^{-}$. Hence, an increase in H in the metal should lead to an increase in H^+ in the nanoscopic layer, because the ultra-thin water layer in contrast to bulk electrolyte has no buffering capability. However, the observed behaviour, i.e. the linear 1:1 correlation between applied and measured potential, is in accordance only with a pinned pH. First results obtained by in operando study of such a hydrogen electrode on palladium indicate that adsorbed CO_2 contamination might play a role in the pH buffering. On iridium, however, significantly lower contamination levels have been observed, but still a linear correlation is found. The role of contamination layers is one aspect to be studied especially with ambient pressure photoelectron spectroscopy (AP-XPS). Also, for the planned combination of emersed and dry electrode AP-XPS will play a crucial role, but a new experimental AP-XPS set-up had to be designed for that and is currently being built up. This research on electrodes in the "dry" will also play a role in the GO department part within the continuation of the excellence cluster RESOLV.

Besides this very fundamental focus on the electrochemical double layer, also more applied aspects of the electrode in the "dry" are investigated. One is to use the changes in potential induced upon switching from humid nitrogen to hydrogen containing atmospheres on the surface of a metal for obtaining information on correlated adsorption energies at the corresponding solid/liquid interface and for providing insight into their role in electrocatalysis of the hydrogen evolution reaction [20, 21]. Another important reaction is of course oxygen reduction, which is a key reaction e.g. in corrosion, coating delamination as well as in fuel cells. Our research could provide very strong indications that the "bare" catalyst particles, which are just covered by adsorbed water in the monolayer range, can be electrochemically active and can provide ORR at high rates. For ORR on a "bare" catalyst particle in a membrane electrode assembly (MEA), protons have to be delivered from the ionomer in the vicinity. It is reported that proton transport can readily occur on the surface of the metallic catalyst, e. g. for Pt via Pt-OH or Pt H. Thus, as supported by our results, catalysts not covered by ionomer may play an important role in the overall ORR activity of the MEA. [1].

6. 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 [22, 23].

Trying to optimize how to carry out high resolution mapping of local hydrogen distribution also of materials with very fine microstructure is a key focus of current activities. This is made difficult by too high back-ground intensities of hydrogen and is tried to be solved by preparing much thinner samples and/or restricting hydrogen loading to an ultra-thin zone at the surface, as far as that is feasible (see p. 68). Especially noteworthy is another also quite 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. This interesting project was unfortunately especially severely delayed by the pandemic, but is now going into a very promising direction.

In another research project (in the Horizon 2020 framework (H2Free)) it is tried to obtain important input data for the modelling of hydrogen release from zinc-alloy and cadmium coated landing gear components. This is a very challenging task and a combination of novel cutting-edge application of Kelvin probe for measuring hydrogen permeation and its distribution inside the materials and thermo desorption analysis is applied. It was found that deformation layers at the surface of the high strength steel are significantly complicating the analysis, leading to a very challenging task.

7. High temperature reactions: from grain boundary reduction to direct reduction of iron ores by hydrogen and ammonia

In cooperation with the Universität Duisburg-Essen and the University of Waterloo also graphene deposition on GaN was investigated. One of the bottlenecks in the implementation of graphene as a transparent electrode in modern opto-electronic devices is the need for complicated and damaging transfer processes of high-quality graphene sheets onto the desired target substrates, such as GaN. By replacing the commonly used hydrogen (H_2) process gas with nitrogen (N_2), it was possible to suppress GaN surface decomposition while simultaneously enabling graphene deposition at < 800 °C in a single-step growth process. At the MPIE mainly characterization via XPS was carried out, demonstrating that the result exceeds the so far best reported values for directly grown graphene on GaN in literature [24].

The investigation of high temperature reactions has been a key expertise within the department for decades. While in the past mainly oxidation processes were investigated in our high-temperature lab, such as in the reporting period the selective oxidation at the grain boundaries of various binary and ternary iron-based alloys [25, 26], the focus is now mainly on investigating the direct reduction of iron ores by hydrogen or ammonia.

Our research on internal oxidation of Fe-Mn-Si alloys [25, 26], which addresses the problem of grain boundary oxidation upon hot rolling of steels, revealed that the extent of the oxidation increases significantly with increasing Si content. Interestingly, an external $(FeO)_{1-x}(MnO)_x$ layer of several tens of nanometres thickness was formed on all the alloys. Nevertheless, the external layer did not impose diffusion inhibition on the oxygen uptake, but this $(FeO)_{1-x}(MnO)_x$ layer was found to have a crucial influence on the kinetics at the studied annealing conditions. As the FeO content of the oxide layer increases with more silicon concentration in the alloy, the layer is suggested to facilitate the O-uptake kinetics [25]. In more fundamental studies on pure iron and binary Fe-Si and Fe-Mn alloys, carried out in our ambient pressure XPS set-up, it was found at low oxygen partial pressure just below the oxidation of iron at the elevated temperature of about 700 °C, that a significantly decreased oxidation behaviour for iron was observed at the surface of the Fe-Si alloys upon cooling, indicating a significantly enhanced oxygen uptake in that case [27].

As concerns the experiments of direct reduction of iron oxides, the high-temperature lab of the GO department is currently re-organized to meet the new requirements. For instance, while in the past the focus was on ultra-low mass changes at the surface and at grain boundaries, now the whole bulk of the sample shows a mass change, which for typical sample sizes is at the limit of our delicate high-sensitive equipment. On the other hand, the high mass sensitivity allows also to measure e.g. small cut single crystal iron oxides. First experiments with such single crystalline materials have been started. First results obtained on more classical pellets show that the relatively easy nucleation of magnetite and the subsequent wüstite as well as the fast solid-state diffusion (most likely inward diffusion of Fe^{2+}) through the iron oxide product layer are the main reasons for the fast reduction kinetics of the hematite to wüstite. The third step, viz. the reduction of wüstite into iron is – during the final 20 % reduction regime – nearly an order of magnitude slower. This effect can be most likely attributed to the sluggish mass transport (particularly of the outbound O solid-state diffusion) through the already formed iron product layers surrounding the wüstite. Near-atomic scale chemical probing reveals the presence of nano-sized Fe-containing transient-state oxides and the accumulation of certain gangue elements i.e. Ti and Na at the metal/oxide interface, both of which are assumed to be another cause for the slow reduction kinetics at the late stages of the wüstite reduction [28].

Atomistic Modelling (S. Wippermann)

In order to surmount materials-related challenges in the context of sustainability, optoelectronics, energy conversion and storage it is of critical importance to understand, predict and control the precise mechanistic details of interfacial chemical reactions and their dynamics at the femtosecond time-scale. The "Atomistic Modelling" group develops and applies accurate simulation techniques in close collaboration with experiments to explore light-matter interaction in nanostructures, electrified interfaces between nanostructures and liquid electrolytes, and their ultrafast dynamics.

Quantum dot solids with targeted properties are of particular interest in this context. Colloidal nano-scale building blocks, e.g. nanocrystals, can be used as "*artificial atoms*" and assembled into quantum dot solids. These nanomaterials located at the borderline between molecules and solids feature intriguing exciton-electron-phonon dynamics, where light can directly affect their fundamental physical properties. Moreover, nanocrystal assemblies provide opportunities to create quantum materials with targeted properties with possible applications, e.g., as next-generation light absorbers for photovoltaics, photoelectrochemistry and power electronics. Fig. 6 shows a prototypical example of a quantum dot solid, consisting of semiconducting core/shell nanocrystals. Either organic molecules or chalcogenidometallalate complexes can be used as "conductive glue", linking the individual building blocks.

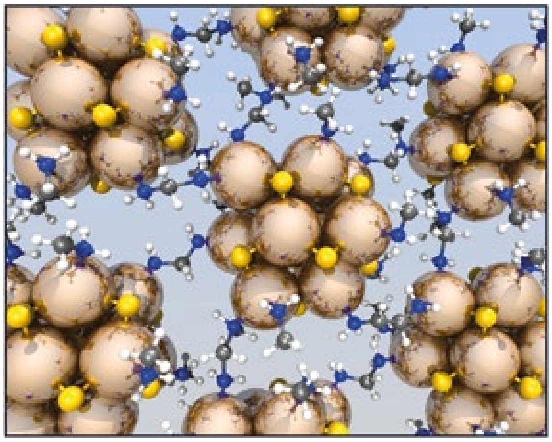


Fig. 6: *Schematic representation of a quantum dot solid, consisting of "magic-sized" nanocrystals assembled into a superlattice. Organic molecules or chalcogenidometallate complexes can be used as surface-selective linkers and "conductive glue", connecting the nanocrystals both mechanically and electrically.*

The Atomistic Modelling Group was awarded a NanoMatFutur-Grant from the Federal Ministry of Education and Research (BMBF) with a total value of 1.8 Mio. Euro 2014 to explore the nano-scale internal interfaces inherent to quantum dot solids and their impact on the emerging macro-scale electronic and optical properties. In addition to our existing collaboration with the Pritzker School for Molecular Engineering at the University of Chicago, two new collaborations were established within the current running period from 2018 – 2021 with the Institute of Basic Science Center for Nanoparticle Research and Center for Nanointegration at the University of Duisburg-Essen, respectively.

III-V semiconductor-based quantum dot solids, consisting of e.g. InP or InGaP nanocrystals, are among the most widely investigated materials systems due to their potentially superior optical properties and lower toxicity, compared to commercially available II-VI quantum dot solids. Whereas narrow emission line widths are readily achieved in II-VI quantum dot solids, III-V systems still suffer from inferior colour purity due to broad emissivity and poor photoluminescence quantum yields. We recently demonstrated [29] that nanocrystal stoichiometry dispersion is a major source of trap states and largely responsible for the observed emission broadening. Whereas II-VI quantum dot solids require only nanocrystal size control to achieve narrow emission, it is necessary to realize in addition nanocrystal stoichiometry control in the case of III-V quantum dot solids.

Anomalously strong temperature-induced shifts of the electronic bandgaps are another important source of emission broadening. In order to reveal the origin of these anomalous shifts, we used so-called magic-sized nanoclusters as atomically precise model systems for nanocrystals with zero dispersion in both size and stoichiometry. Tantalizingly, approaches that are commonly employed to accurately calculate temperature-dependent bandgaps in bulk materials have been known to predict qualitatively wrong results for nanocrystals since more than a decade ago. We conjectured that these shortcomings of traditional approaches are caused by their inability to take exciton-phonon coupling into account. We therefore developed a novel approach that allows us to accurately compute temperature-induced band gap shifts using constrained ab initio molecular dynamics (AIMD) simulations on the excited state potential energy surface and atomistic thermodynamics, where the band gap is computed as the Gibbs free energy of exciton formation. In contrast to existing methods, our approach explicitly takes the fully anharmonic exciton-phonon coupling into account.

We revealed [30] that the experimentally observed anomalous colour shifts with temperature are caused by excitonic bond-softening: in nanocrystals, the excitons are distributed over only a small number of atoms due to the strong quantum confinement. In consequence, the occupation of antibonding states due to the presence of the excitons significantly weakens the interatomic bonds, leading to a pronounced exciton-induced red shift of the phonon density of states (PDOS). This shift is almost two orders of magnitudes larger than the corresponding one observed in bulk materials. The red-shifted PDOS in turn is responsible for the anomalous bandgap shift due to its impact on the Gibbs free energy of exciton formation. Our results underline the importance of explicitly considering exciton-electron-phonon coupling in nanostructures and suggest how to design systems with improved optical properties.

Another fascinating example of ultrafast light-matter interactions is the precise optical control of structural transitions at the “quantum limit” in the regime of directed and deterministic nuclear motion. Chemical composition, pressure and temperature are commonly utilized to control and tune the properties of materials. Beyond these established concepts, here we explore how intense light fields and coherent control schemes inspired by concepts from femtochemistry can be used to guide the nuclear and electronic degrees of freedom through their complex multi-dimensional potential energy landscape into new states of matter.

To this purpose, the Atomistic Modelling Group established a new collaboration between the DFG FOR 1700 research group (see p. 93), the Institute of Basic Science Center for Low Dimensional Electronic Systems and the Max Planck Institute for Biophysical Systems. We use the atomic wire array known to form on the Si(111)-(4x1) In surface as an atomically precise model system in order to develop techniques for observing and controlling chemical bond-making and bond-breaking processes at the femtosecond time scale. Each atomic wire on this surface consists of two coupled monoatomic chains. At temperatures below T_C = 120 K, both chains undergo a period-doubling metal-insulator transition into a charge density wave (CDW) phase, driven by a triple-band Peierls instability. Thereby, formerly delocalized metallic states now become localized and form covalent bonds. This transition is of 1st order, hampered by an energy barrier. We demonstrated that the insulating and the metallic phases are able to coexist at temperatures close to T_C, giving rise to a phenomenon called electronic phase separation (EPS) and the formation of novel types of interfaces, such as metal-CDW junctions [31].

The transition itself is driven by multiple soft phonons with a strong coupling between electronic and lattice degrees of freedom. Due to the coupling between the two monoatomic chains, different superpositions of these phonons transform the chains into structurally distinct but energetically degenerate CDW states. Moreover, the coupling introduces a band inversion. As a consequence, the CDW phase supports fundamental excitations that take the form of interfaces between these degenerate states, and that feature topological properties with associated electronic chiral edge states inside the CDW band gap. In analogy to knots in a string, these topological states can be used to store and even process information at the molecular scale.

For all these reasons, atomic wires are promising targets in order to (i) explore the dynamics of chemical bond formation at the femtosecond time scale and (ii) develop, implement and test coherent optical control schemes using femtosecond laser pulse sequences. Based on our constrained AIMD approach, we design suitable pulse sequences and simulate the induced reaction dynamics. Depending on the targeted optical transition, a specific CDW state can be transformed e.g. into another structurally distinct CDW state or a supercooled metallic state. Fig. 7 shows a schematic outline of these concepts.

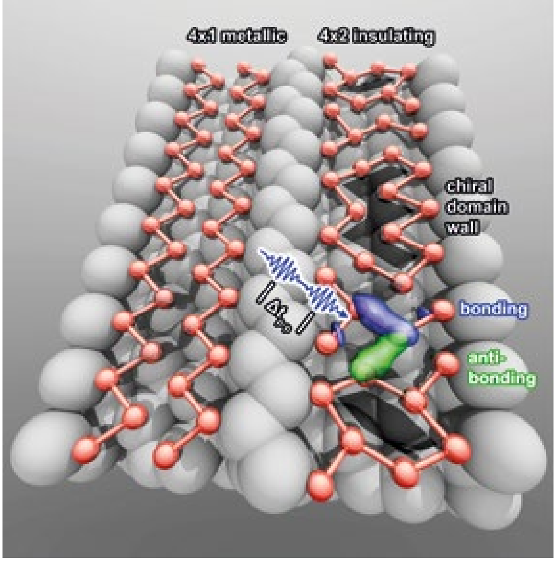


Fig. 7: *Schematic representation of structural motifs observed in the atomic wire array formed at the Si(111)-In surface. At room temperature, each indium wire consists of two coupled monoatomic indium zigzag chains. Below T_C = 120 K, the wires undergo a period doubling triple band Peierls transition into one of multiple possible charge density wave (CDW) states. The coupling between the monoatomic chains induces an electronic band inversion, leading to the formation of chiral topological edge states at domain boundaries between different CDW states. Exciting specific optical transitions by fs laserpulse sequences with carefully timed delays Δt_{P-P} allow us to form or dissolve specific chemical bonds.*

Extending these concepts, we recently started to explore the interaction of nanostructures with liquid electrolytes. Emerging energy conversion and storage technologies, such as artificial photosynthesis and power-to-X devices, critically depend on precisely engineering the chemical dynamics, reactivity and selectivity of interfaces between optically excited or electrified nanostructures and liquid electrolytes. Based on the Modern Theory of Polarization, we develop methods to incorporate electric fields in density-functional theory (DFT) and apply them to answer fundamental questions in the thermodynamics and transformation of electrochemical semiconductor-liquid interfaces.

In electrochemical experiments, the applied potential is held at a value that is constant on average at the macro-scale, but electronic and ionic charges fluctuate and transfer freely into and out of the region close to the interface, that is targeted by our simulations. In consequence, when studying elementary processes at electrified interfaces by DFT, we must treat the local surface charge not as a constant, but as a thermodynamic degree of freedom with temperature-dependent fluctuations. In collaboration with the CM department and building on our finite electric field techniques, we recently introduced a “thermopotentiostat”: a novel approach to control the electrode potential that can be used equally well to perform empirical or ab initio molecular dynamics simulations [32]. By design, (i) it satisfies the fluctuation-dissipation theorem exactly and is thus cleanly embedded into thermodynamic theory, (ii) requires only quantities that are either readily accessible in DFT codes or are known from the specific setup, and (iii) it is straightforward to include in any existing DFT code.

In order to demonstrate the performance of our thermopotentiostat approach, we considered a topic that had recently gained a lot of attention. Recent experiments performed in the A. Geim group (University of Manchester) showed that a water film confined to a few nm thickness changes its dielectric behaviour from the bulk dielectric constant of 80 down to 2. Thus, the presence of solid-water interfaces appears to modify the dielectric response of water from a highly polarizable medium, which is considered to be the origin of the unique solvation behaviour of water, down to a response that is close to the vacuum dielectric constant. Understanding and being able to qualitatively describe this mechanism is crucial, since interfacial water is omnipresent and electrochemical reactions in particular occur within the interfacial water region.

Because of the relevance of this question in fields as diverse as electrochemistry, corrosion and electrocatalysis, multiple computational studies addressed dielectric properties of nanoconfined water. These studies generally rely on Kirkwood-Fröhlich theory, using the variance of the total dipole moment fluctuations per volume, or on the theory of polarization fluctuations. However, the exact location of the boundary between the electrode and the dielectric is ill-defined. Past studies therefore reported only dipole fluctuations perpendicular to the electrode surface, but not the dielectric constant itself.

Our thermopotentiostat approach allows us to address this question directly, since our computational setup shown in Fig. 8a exactly reproduces the experimental situation. Here, liquid water is confined between two electrodes where the electrode charge is actively controlled by our thermopotentiostat. Fig. 8b shows the calculated static dielectric constant as a function of the water layer thickness, compared to the experimental data from the Geim group. Consistent with the measurements, our results display a pronounced decrease of the dielectric constant compared to the static dielectric constant of liquid bulk water, that persists for electrode separations exceeding 100 nm.

In order to understand the origin of the decreasing dielectric constant with decreasing electrode separation, we computed the local inverse static dielectric constant as a function of the normal distance to the electrode surface, cf. Fig. 8c. At the position of the electrode surface, the inverse dielectric constant drops sharply and intersects the water bulk value at ~ 3 Angstrom above the surface. With further increasing distance, it assumes negative values for interfacial water and then approaches the bulk water value in an oscillatory fashion. Beyond a normal distance of ~ 9 Angstrom, the dielectric constant of bulk liquid water is recovered. Our results demonstrate that the region with modified dielectric properties is closely confined to the region of interfacial water. Introducing a continuum surrogate model informed by the dielectric profile shown in Fig. 8c, we demonstrated that the local dielectric properties of water close to the interface are indeed responsible for the observed reduction of nanoconfined water’s

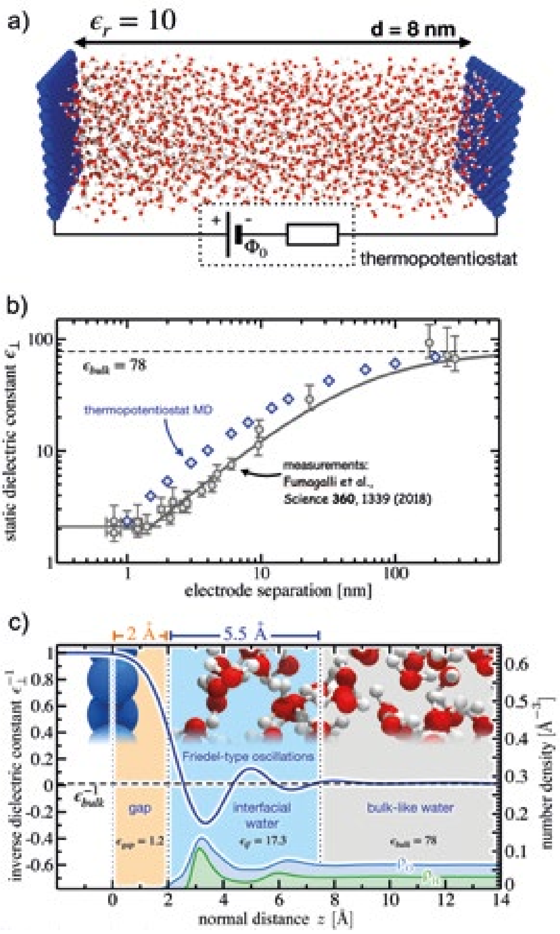


Fig. 8: ***a)*** *Computational setup, consisting of liquid water confined between two electrodes. The electrode charge is actively controlled by our thermopotentiostat.* ***b)*** *Static dielectric constant for TIP3P water as a function of electrode separation, calculated using thermopotentiostat molecular dynamics (MD). Quantitative differences with respect to the measurements encode chemical information on the specific surfaces used in the experiments, as our model is based on generic hydrophobic electrodes. Experimental data reproduced with permission from Science 360 (2018) 1339.* ***c)*** *Local inverse dielectric profile and O/H number density profiles. Reproduced with permission from the American Physical Society [4].*

dielectric constant compared to the static dielectric constant of bulk water [32].

This intriguing behaviour of the polarization density within interfacial water resembles the physics of Friedel oscillations at metallic surfaces, albeit with a much stronger amplitude. The wavelength of the oscillations corresponds to the size of the water molecules. A negative local dielectric constant implies a net attractive force between like charges. On-going research builds on these findings to explore the formation and structure of electrochemical double layers and charge transfer reactions at electrified solid-water interfaces.

We note that the calculation of dielectric profiles from polarization fluctuations requires hundreds of nanoseconds of statistical sampling, in practice enforcing the use of classical molecular dynamics. In contrast, the use of stochastic canonical sampling in our thermopotentiostat technique in conjunction with finite electric field methods allows us to rely purely on thermodynamic averages rather than variances. Thus, the required computational time to converge the dielectric profiles is reduced by more than two orders of magnitude, placing these types of calculations now well within reach of *ab initio* molecular dynamics simulations.

These research activities focus on solving outstanding fundamental open problems in the context of light-matter interaction in nanostructures, low dimensional electronic systems and electrified interfaces.

Our activities benefit from mutual insights obtained in different areas of interface chemistry and surface science research conducted at the MPIE. In order to foster also exchange at an international level, in February 2019 with the FOR 1700 research group (see p. 93). we conducted a three-day workshop at Ringberg Castle on “Surface Science: The Past, Present and Future”, in order to bring together leading scientists from the areas of low dimensional electronic systems, surface spectroscopy and strongly correlated systems. For April 2020, together with the CM department we planned a three-day workshop at Ringberg Castle on “Electrified solid/water interfaces – theory meets experiment”, inviting leading scientists from the fields of electrochemistry, solvation and spectroscopy. Due to the CoViD-19 situation, this workshop has been rescheduled to March 2022.

Interface Spectroscopy (A. Erbe)

This group was active as a guest group until end of 2019. Strong activities of that group were in the field of optical methods development. In collaboration with the former research group “Interaction Forces and Functional Materials” of M. Valtiner (now professor at TU Wien, Austria) a novel method for the analysis of data acquired in a typical surface force apparatus experiment has been developed. This method adapted known matrix methods for analysing reflectivity spectra with the specific requirements of the optics of surface force apparatus measurements. This method helps to overcome limitations in the approximations of classical methods [33].

In a collaboration between the MPIE, the University of Pisa, the Italian National Research Council and the Indian Institute of Technology Dhanbad, a novel microwave-based polymerisation technique was used to make poly(styrene) microspheres with few μm diameter that contained a lasing dye. The resulting particles have been shown to be amongst the world’s smallest polymer-based whispering gallery mode supporting micro-resonators, and are suitable for sensing the environment at the particle / solution interface via changes in the interfacial refractive index [34].

In a collaboration with the Norwegian University of Science and Technology, infrared imaging was used to image subsurface modifications of silicon, which were prepared by the partner with a non-linear optical laser writing technique [35].

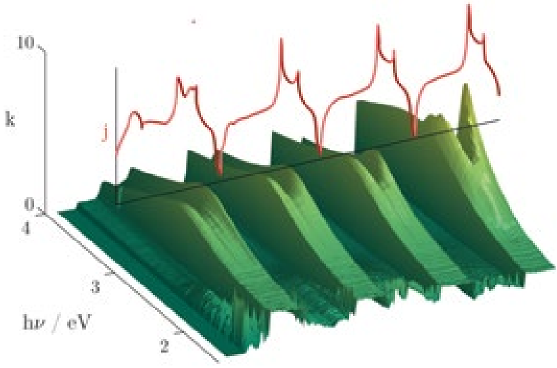


Fig. 9: *Results of in situ electrochemical spectroscopic ellipsometry. The positive/negative peaks in the current density (j) indicate formation/reduction of thin oxide layers. The measured k-spectra illustrated as 3D plot indicate reversible changes in the electronic structure at the onset of the oxygen evolution reaction.*

Another topic was the Application of spectroscopic techniques for investigation of electrochemical and corrosion phenomena. Traditionally, the “Interface Spectroscopy” group has used optical techniques for materials characterisation. In the search for novel abundant catalytic materials for electrochemical water splitting the oxide layer growth on manganese during electrochemical oxidation and oxygen evolution reaction (OER) in basic electrolyte was thoroughly studied, in cooperation with M. Rabe [36]. Using Raman and ellipsometric in situ spectroscopy stable oxide films containing mostly α-MnO2 were observed at the onset of OER (Fig. 9). High Mn dissolution rates were measured during OER, limiting the applicability as catalyst. However, still a stationary stable, highly disordered phase was found, containing MnO_6 tetrahedra. In a PhD thesis, which was finalised in the reporting period, zinc corrosion was investigated in detail by spectroscopic methods with dif-

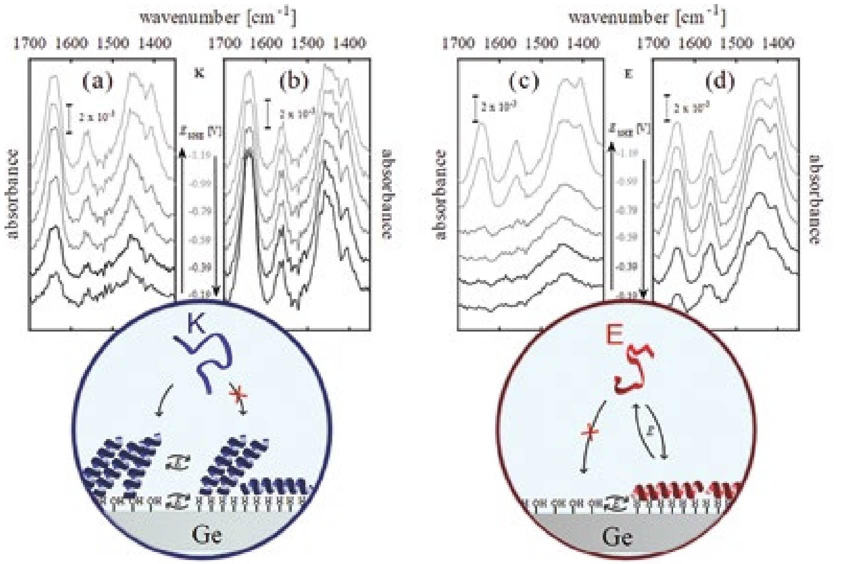


Fig. 10: *Results of in situ ATR-IR spectroscopy to study electro-responsive smart Ge interfaces. The detailed analysis of potential dependent amide I' peaks (at ca. 1650 cm^{-1}) and the Ge-D stretching band (shoulder at 1405 cm^{-1}) in the spectra (a-d) revealed mechanistic details of reversible adsorption and orientation changes of the helical model peptides.*

ferent collaborators. Besides an imaging of the spatial distribution of the corrosion products, the detection of a hydrogen saturated oxygen vacancy as an important defect in the initial corrosion products of zinc in sea water stands out [37].

Finally, also the work within this group on Surface chemistry of reactive materials should be mentioned. As a side result of a project on zinc pre-treatment with biopolymer based coatings, a switch in the surface appearance between black and white when changing the electrode potential of zinc coated with a gelatine-based coating was achieved [38].

In a study of the surface modification of copper with organic alkyl thiols, solvent specific adsorbate structures were found. In particular, the C-S bond in the thiol molecule was found to be cleaved through the strong Cu-S interaction [39]. As part of a systematic study of the interaction of model organic coatings with metal substrates, the cathodic delamination rates of differently surface bound poly(styrene) coatings have been compared [40]. Healing of coating defects upon damage has been an important focus of the work in the department. In one project, the inclusion into a pre-treatment of a cyclic oligosaccharide incorporating a film-forming corrosion inhibitor has been shown to lead to healing of defects in an organic model coating on zinc [12].

Spectroscopy at Electrochemical Interfaces (M. Rabe)

The early career research group “Spectroscopy at Electrochemical Interfaces” was newly set up in 2020 and is co-funded by the MPIE and the cluster of excellence ‘Ruhr explores solvation’ RESOLV (see p. 86). It partly stands in the tradition of the “Optical Spectroscopy Group” of A. Erbe, and now develops a new independent research profile. In the group optical interface spectroscopy methods are employed for exploring interface characteristics and dynamic processes. Ongoing and future research activities specifically focus on interface solvation, a fundamental phenomenon occurring whenever a liquid phase -especially water- terminates at a solid interface. This specific structural arrangement of solvent molecules on interfaces plays vital roles for instance in electrochemical applications, biological reactions or atmospheric processes, which require a fundamental understanding. Furthermore, electrochemical *in situ* spectroscopy is applied for the study of OER catalysts employed in alkaline water electrolysis for the production of green hydrogen (for more details on future and ongoing projects see p. 45).

In several cooperation projects plain or layer covered metallic substrates or alloys were studied employing the expertise in spectroscopic ellipsometry (SE). In a collaboration with the Faculty of Chemistry of Silesian University of Technology in Gliwice, Poland, conversion coatings formed by anodization in alcohols on top of galvanic Zn-Ni alloy coatings on steel were studied [41]. The coatings were composed of mixed oxide-alkoxides and featured high corrosion resistance and optical colouration. The detailed analysis of the SE data revealed that the visible colour varies with the layer thickness of the coating, which was a mixed oxide-alkoxide layer and can be controlled by the anodization process.

In an internal cooperation with the “Corrosion” group the formation of water layers on various noble metals in humidified atmospheres up to 98 % rh are examined. For instance, the layers formed under these circumstances on Pd are ultrathin < 1 nm [1], but electrochemical reactions underneath such layers play important roles in technically relevant processes such as electrolysis, fuel cells and atmospheric corrosion. Currently, similar studies on Ir and Au are ongoing.

In a project collaboration with the VDEh-Betriebsforschungsinstitut GmbH (BFI), the optical properties of steel samples of varying composition are studied by SE. Aim of the BFI-led project is to develop a system for the in-line measurement of the steel composition directly in the liquid melt by reflection spectroscopy. Interestingly, variation of the concentrations of specific elements such as Ni and Cr have been found to have a significant influence on the reflectivity of the steel samples at normal incidence, which supposedly can be exploited for the planned measurement principle. The technical development and pilot implementation at BFI is ongoing and further supported by our group.

In order to understand and design electro responsive ‘smart’ interfaces, research has been conducted exploring the interactions of α-helical peptides with interfaces. Following up on earlier work, performed in the GO department that revealed details of the electrochemically triggered reduction of germanium surface termination, this reversible termination change was employed for a hydrophobic/hydrophilic switchable, ‘smart’ interface. By employing *in situ* attenuated total reflection infrared (ATR-IR) spectroscopy it was shown that the hydrophobicity switch can reversibly trigger ad-/desorption as well as orientation change of amphipathic model peptides (Fig. 10). The observed process (ad-/desorption or orientation change) depends on the adsorbates charge distribution, which indicates that a sensitive balance between hydrophobic and electrostatic interactions governs the surface attachment.

Chemometric methods are developed and implemented in the group to improve the analysis of complex or large multivariate spectroscopic data. A hard modelling multivariate curve resolution (MCR) approach was implemented to resolve multivariate spectral data with several components lying closely together in terms of their peak positions (as function of photon energy or wavenumber), but with individual dependencies on a specific control variable (such as temperature, pH, potential, etc.). The approach is based on empirical or physical transition models chosen by the analyst that describe the dependency of the spectral intensity on the control variable. Within several research projects in the GO department, this approach has been employed and advanced. For instance, for the analysis of *in situ* ATR-IR spectra of germanium desolvation and photoluminescence spectra of corrosion products on zinc [37]. Most recently, the implementation was extended to allow a convenient application to complex data sets with virtually unlimited spectral components and an individual choice of transition models. This development significantly eases the application of the method for different spectroscopic methods in diverse fields. It is available as open source library [42]. In a collaboration with Leiden University a method was developed and implemented for the analysis of multivariate titration curves of metal binding of multicore peptide-metal complexes. By this method circular dichroism spectroscopy data was analysed to examine the thermodynamics of folding of the trinuclear Ni(II) and Cu(II) complexes of the designed α-helical peptide trimer HisAD [43]. Unexpectedly, it was found that the titration data can only be explained by a 3-state model and it was shown that this is caused by a mononuclear intermediate in the folding pathway.

Dynamic Electrocatalytic Interfaces (O. Kasian)

This is the former group of K. Mayrhofer who left the MPIE already in 2015, but which was still operating until now, first still headed by K. Mayrhofer and since 2019 by O. Kasian. O. Kasian holds the position of head of a

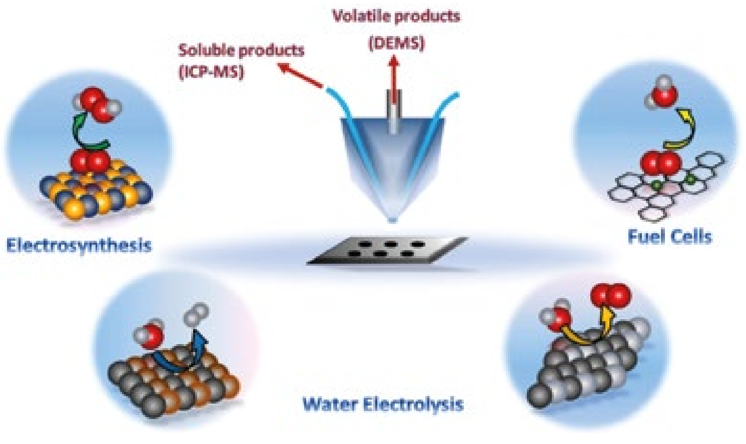


Fig. 11: *Schematic overview of the applications of a flow cell coupled to analytics for simultaneous detection of soluble and volatile reaction products and intermediates in energy conversion related applications such as fuel cells and electrolysis. On-line ICP-MS (inductively coupled plasma mass-spectrometry) allows precise quantification of dissolution in electrochemistry, while DEMS (differential electrochemical mass spectrometry) enables qualitative analysis of gaseous species formed during the reaction.*

Young Investigator Group at the Helmholtz Institute Berlin in collaboration with the Helmholtz Institute Erlangen-Nürnberg for Renewable Energy. At the MPIE she was offered to head the guest group on "Electrocatalysis". The research is focused on the dynamic transformations of the catalytic surfaces under the reaction conditions. The group develops nanostructured model thin film surfaces and explores their structural and compositional changes induced by the catalytic processes and the effect of such transformations on the mechanism and kinetics of the reactions in electrocatalysis. This is achieved by combination of various *ex situ* and *in situ* methods.

In fact, until 2020 a part of the research was still focussed on K. Mayrhofer´s activities, such as on oxygen reduction [44, 45], hydrogen peroxide synthesis [46], CO_2 reduction [47], stability of catalysts [45, 48, 49]. hydrogen evolution reaction [20] and oxygen evolution reaction [50].

The activities of O. Kasian at the MPIE were mainly related to water splitting.

Understanding the fundamentals of electrocatalytic reactions is of importance for the development of efficient and durable energy conversion and storage devices. In such devices the target reactions are often accompanied by unwanted degradation or deactivation of the catalysts. These reactions are often ongoing via formation of common intermediates, which makes mechanistic studies very complex and requires employment of highly sensitive analytics. In the "Dynamic Electrocatalytic Interfaces " group we have developed an approach to distinguish between intermediates and products of various reactions combining isotope labelling with online electrochemical and inductively coupled plasma mass spectrometry [51 and Fig.11].

Recently, employing this technique the group aided in understanding of the water splitting mechanism on iridium-based oxides [51-54], a pivotal and timely topic in the 'green' hydrogen production technology. Iridium oxide anodes are used to catalyse formation of oxygen from water, because of their superior corrosion resistance and relatively high catalytic activity. Nevertheless, even iridium undergoes dissolution in the harsh conditions of the oxygen evolution. This is especially crucial for catalysts with high reactivity, such as hydrous oxides. Our approach allowed us to provide a quantitative assessment of the degree of lattice oxygen participation in the oxygen evolution reaction and the associated degradation of the Ir-oxides. The data obtained on ^{18}O-labeled catalysts reveal that amorphous hydrous oxides are prone to degradation via so-called 'lattice oxygen evolution mechanism', in which oxygen molecule can be formed directly from the oxide lattice atoms without water discharge. This oxygen evolution mechanism results in faster degradation and dissolution of Ir. In compact oxide structures, e.g. rutile IrO_2 such mechanism is less probable.

Overall our results provide a contribution to the fundamental understanding of the exceptional stability of Ir-oxides towards the oxygen evolution reaction. The proposed approach to a quantitative assessment of the degree of lattice oxygen participation in the oxygen evolution reaction can be further applied to other state-of-the-art catalyst systems used in fuel cells or electrolysers.

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Department of Microstructure Physics and Alloy Design (MA)

D. Raabe

Introduction

Scientific mission

We study microstructures and their influence on the properties of materials, mostly metals. Microstructure comprises the structure, size, dimension, patterning, and chemistry of all lattice defects including vacancies, dislocations, and interfaces. We study individual defects such as single vacancies (with Field Ion Microscopy and atomistic modelling) [1–3] and also large statistical defect ensembles such as light years of entangled dislocation lines (for instance by X-ray diffraction and crystal plasticity modelling) [4–7].

Microstructure affects all materials, from pure single crystals [8, 9] to complex engineering alloys [10–13]. It can change, by orders of magnitude, a material's mechanical behaviour (e.g. strength, ductility), electrochemical response (e.g. corrosion, charging behaviour), and functional properties (e.g. magnetic hysteresis, electrical conductivity).

For tailoring microstructures and chemistry, we work on alloy design [14–18], metallurgical processing [19–21], combinatorial synthesis [21–25], sustainable production [26–29], and additive manufacturing [30–36].

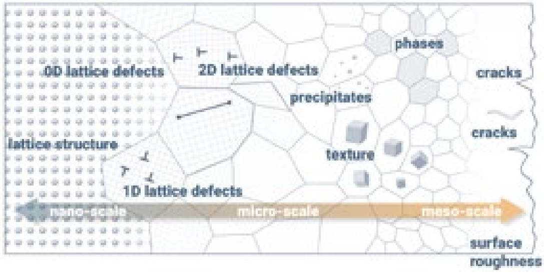

Fig. 1: *Microstructure cosmos, consisting of a range of lattice defects and their chemical decoration features.*

Our main analysis tools are computational materials science [37–39], machine learning [3, 13, 40–42] as well as multiscale and multi-probe characterization [18, 43–49].

With this expertise we have developed a knowledge-based as opposed to the traditional try-and-error-approach to the development of new materials, microstructures, processes, and property combinations, often by reconciling sometimes antagonistic features such as mechanical strength, ductility and soft magnetic behaviours [20, 50–54].

Impact on society

Since the dawn of mankind, materials have been the backbone of human society. Today, they are indispensable in the fields of energy, industry, transport, health, construction, safety, and manufacturing. With >2 billion tons produced every year, metals stand for massive economic growth, job safety, and wealth increase. Due to the sheer quantities produced and used, they also play a central role in sustainability.

Currently, we enter from the age of linear industry into a circular and digitalized economy. This offers huge opportunities to revolutionize production, transport, and energy supply. These changes affect the daily lives of billions of people. Advanced metallic alloys, their production, use, and recycling are key to this transition, as they can help enabling a carbon-free, digitalized and electrified industrial and urban future.

Metals play a twofold role in that context. On the one hand they enable many products and processes through which energy can be saved and greenhouse gas emissions can be reduced. Examples are thermoelectrics for waste heat harvesting [55–59], high-strength alloys for reducing the weight of vehicles we discuss here cases where metastable phases are not coincidentally inherited from processing, but rather are engineered. Specifically, we aim at compositional (partitioning [20, 60–63], or magnetic materials [54, 64–66] for electrical engines. On the other hand, they are the highest single source of greenhouse gas emissions, particularly due to synthesis, which often involves carbon as a reductant, making metallurgy the biggest single cause for global warming [27–29].

Therefore, we devote our efforts to understand, invent, and enable advanced materials and processes for a sustainable and safe future [26–29].

Fields of Special Methodological Expertise

Computational materials science

Our expertise in this field lies in the theory of micromechanics and its non-linear interplay with chemistry and phase transformations [5, 55–58]. Recently, we have also started to include the interaction of micromechanics and redox reactions in our simulations, such as needed to describe material decay, corrosion, and reduction processes in energy conversion applications, harsh environmental conditions and metallurgical sustainability.

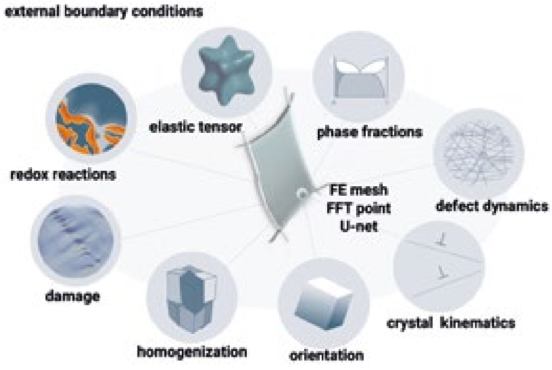

Fig. 2: *Microstructure simulation considering mechanics, chemistry, phase transformations, and redox reactions.*

We have cast our research experience and simulation codes accumulated over more than 25 years into the software package DAMASK [5, 37, 59–62], a free material simulation kit for modelling multi-physics crystal plasticity, thermal, phase transformation, and damage phenomena from the single crystal up to the component scale (Fig. 2, see also p. 73). It is employed by hundreds of academic users and companies worldwide (https://damask.mpie.de). We use it for both, predicting microstructure evolution and the resulting properties on the one hand and for boundary condition treatment of experiments on the other hand. This approach enables us to render microstructure research quantitatively.

Multiscale and multi-probe microstructure characterization

Our expertise in this domain lies in applying fully cor-relative atomic-scale and mesoscale probing of struc-ture, defects and chemistry to the exactly same mate-rial position, to jointly probe structural, chemical, and property features e.g. of chemical decoration and transformation phenomena at internal interfaces, environmental degradation, dislocations, or even single vacancies[18, 43–49]. We use combinations of atom probe tomography (APT) [63, 64], electron channelling contrast imaging under controlled diffraction condi-tions (ECCI) [65–68], 3D electron imaging and backscatter diffraction (EBSD) [69–72], cross-correlation EBSD [73, 74], and field ion microscopy (FIM) [1–3], often coupled with theory and machine learning, for enhanced quantification of the data. We apply such correlative multi-probe methods to a range of materials, from well-defined single crystals up to complex engineering metallic materials. This approach enabled discoveries such as low-dimensional trans-formations of chemically decorated dislocation core regions [75, 76], interfacial spinodal-like chemical decomposition effects at interfaces [12, 77, 78], or partitioning phenomena [10, 79–82] among several types of adjacent phases and lattice defects.

Increasing focus in characterisation lies in considering environmental degradation of materials. This is a particularly challenging task when it comes to the joint characterization of microstructures, damage features, and the reactants and reactions that are causing the degradation, involving for instance hydrogen (to study hydrogen embrittlement), oxygen (to study corrosion), and light reactive elements such as lithium (to study batteries) [13, 26, 45, 46, 83–85]. Especially hydrogen is extremely hard to image and once being mapped one must make sure that it is the hydrogen that was charged in an experiment by purpose and not the hydrogen that had intruded due to contaminated experimental conditions. We have therefore established a cryogenic and ultra-high vacuum workflow that combines a reaction and charging laboratory hub with plasma focused ion beam, electron optical, and atom probe tomography characterization instruments (see p. 47 & 50).

Alloy and process design

In this fields we apply our approaches to make materials that have property profiles with often conflicting features. Examples are alloys with high mechanical strength on the one hand and good ductility, fracture toughness, thermoelectric performance, hydrogen embrittlement resistance, or functional properties on the other hand [14–18].

As one example to solve the fundamental conflict between strength and ductility we introduced a gener-alized metastability alloy design principle [14, 79, 86]. This means that the thermodynamic stability of the dominant matrix phase or of a chemically decorated confined region (such as a single lattice defect or interface region) of an alloy is compositionally adjusted in such a way that athermal transformation mecha-nisms (such as twinning and martensite formation which both profoundly increase the material's strength) are activated in a specific window of the stress-strain regime where they are needed to coun-teract localization and micro-damage inside the alloy. This metastability alloy design concept has led to a number of discoveries of new materials with excep-tional load-bearing capacity paired with high damage tolerance [35, 54, 95, 97–100].

Another example is in magnetic alloys [12, 48, 87–89]: regarding the combination of strength and good func-tional properties we develop high strength soft mag-netic materials, for instance by utilising spinodal de-composition or alloys with high volume fraction of precipitates. Another direction lies in developing alloys and coatings with specific compositions and micro-structures that have a high resistance to hydrogen embrittlement and corrosion [26, 90–92].

Processes, mechanisms, and materials for sustainability and a circular economy

The microstructure-centred approach of the department enables us to address our latest research quest, namely, to identify pathways towards enhanced sustainability of metallic materials, in areas which include reduced-CO_2 primary production, recycling of metals, scrap-compatible alloy design, contaminant- and hydrogen tolerance of alloys, hydrogen-plasma based reduction, electrolysis for the reduction of oxides, and H-based direct reduction of iron ores [26–29].

For this purpose, we have designed and modified a number of laboratory-scale reactors in which corresponding experiments can be conducted, under well-controlled reactive boundary conditions and temperature control as well as permanent in-operando monitoring through mass spectrometry. These experiments are conducted in close cooperation with the group of M. Rohwerder at the GO department (see p. 125).

Some topics are currently pursued with high activity, namely, H-based direct reduction of iron oxides, H-plasma-based reduction (see p. Ma group), and the design of alloys that can tolerate highest possible scrap and thus impurity fractions.

These projects show two interesting trends, a more specific and a more general one: Firstly, there are numerous fundamental research questions that can only be successfully addressed when embracing methods from process metallurgy and physical metallurgy together. An example is the immense role of microstructure, fracture, and porosity on the direct reduction kinetics of solid oxide minerals exposed to hydrogen or hydrogen carriers [27].

Secondly, on more general grounds, there are multiple unexplored phenomena and basic research questions in the field of sustainable metallurgy [29]. This means that there is much room for new discoveries and the leverage of such discoveries on reducing the energy consumption and greenhouse gas emissions of these industries is potentially very large, equipping the urgent need for improved sustainability of the metallurgical sector with novel core competences. This becomes clear when recalling that about one-third of all industrial greenhouse gas emissions come from iron and steel making alone [29].

Common scientific motif

The common scientific motif behind the research activities in the department is the interplay between all the defects that make up an alloy's microstructure and their local chemistry [93]. For revealing the underlying scientific laws of these interactions we conduct well-designed experiments and run them in concert with predictive simulations [5, 37, 67, 71, 108]. We use the resulting insights for engi-neering applications, particularly for inventing ad-vanced alloys and more metallurgical processes. More specific, the aim is the physics-based design of mate-rials with superior properties and sustainable process-es for the fields of energy, mobility, infrastructures, and health.

Material choices

We aim to understand the fundamental relationships between specific thermodynamic and kinetic features of materials and the evolution of microstructure and thus their effects on mechanical and functional properties. We therefore select, synthesize, process, and probe materials along specific intrinsic property gradients, such as their phase (meta-)stability, solid solution content, stacking fault energy, (athermal) transformation behaviour, magnetic hysteresis, or chemical reactivity. Along this systematics we work on the fundamentals of the relations between synthesis, microstructure, and properties of often complex and nanostructured materials. Focus is on metallic alloys such as aluminium, titanium, steels, high and medium entropy alloys, superalloys, magnesium, and magnetic and thermoelectric alloys.

Department structure and research groups

The department structure and organization reflects our understanding of fundamental yet highly flexible research. Some of the research groups pursue long-term visions of high strategic and methodological relevance for the department's mission. Some other groups are non-permanent, and they are usually extramurally funded. This helps to rapidly establish new initiatives and to provide opportunities to young science leaders to pursue their own ideas and grow new initiatives (Fig. 3).

These non-permanent groups establish not only hubs for new research directions but they are also career vehicles for postdoctoral researchers who attract extramural funding, which allows them to establish own research initiatives. Funding agencies addressed for such initiatives are for instance the Max Planck -Fraunhofer collaboration scheme or the European Research Council, German Research Foundation, Federal Ministry of Education and Research (BMBF), and Volkswagen Foundation. These groups act as career platforms and rapid idea incubators, initiating new topics of highest novelty, quality, and scientific success. Most former group leaders of these initiatives have gained faculty positions at leading institutions around the globe.

Another category of groups is placed between the departments and between the MPIE and partner institutions elsewhere. These groups are often also funded by extramural third-party funds or by partnership programs of the Max Planck Society (MPG). They establish new

Fig. 3: *Research Groups in the Department Microstructure Physics and Alloy Design, together with Interdepartmental and Partner Groups.*

research fields which are placed between the individual departments and thus form centres for intense cross-disciplinary research, tapping competences from all departments and from centres outside of the institute. The interdepartmental and partner groups present their work in separate sections (see p. 23 - 35).

Long-term research groups

The long term research groups in the department work on Atom Probe Tomography (B. Gault), Computational Sustainable Metallurgy (J. Mianroodi), Mechanism-based Alloy Design (D. Ponge), Microscopy and Diffrac-tion (S. Zaefferer), and Theory and Simulation (F. Roters).

Atom Probe Tomography (B. Gault)

Atom Probe Tomography (APT) is a high-resolution characterization technique that provides three-dimensional elemental mapping with near-atomic resolution. Insights from APT help understand phase formation and transformations, segregation at interfaces, and partitioning between phases. The group focuses on applying this burgeoning microscopy and microanalysis technique to a wide range of advanced materials, with an emphasis on correlating the information gleaned from APT with other experimental and computational techniques [49, 101, 109–113]. The group has strong ties with numerous other groups within MPIE, in particular with the group for Mechanism-based Alloy Design, and across departments, with the Computational Phase Studies and the independent Nanoanalytics and Interfaces research group.

The group has operated since the installation of a local electrode atom probe Cameca LEAP 3000X HR in 2009. In August 2015, a second instrument, a LEAP 5000 XS was the first of its kind installed in the world, followed in February 2017 by a LEAP 5000 XR. The LEAP 3000 instrument was replaced in 2019 by another LEAP 5000 XR. These state-of-the-art instruments offer a wide field-of-view, high detection efficiency, and new generation of UV lasers. These instruments are complemented by two FEI Helios Dual Beam SEM/FIB (600/600i) and a FEI Helios PFIB.

The two LEAP 5000 XS and XR instruments are part of a world unique setup allowing for controlled transport of APT specimens from a glovebox to a scanning-electron microscope / focused ion beam to one of the two LEAPs via an ultra-high-vacuum suitcase. Transport of specimens can also be performed at cryogenic temperatures. This infrastructure was funded jointly by the BMBF and the MPG.

Computational Sustainable Metallurgy (J. Mianroodi)

The impact of humans on the environment and climate has long been scientific fact. Acceptance of this fact in the non-scientific world has finally reached the point where many societies and governments have started to adopt policy and to implement measures geared toward reduction or even elimination of this impact. Prominent examples of this include the idea of a climate-neutral, sustainable, and at least partially circular economy and production.

A number of scientific and technological challenges emerge from these considerations for the field of material engineering, metallurgy, steel production, energy storage, battery technology, and recycling. Solving these outstanding scientific challenges requires proper understanding of the underlying mechanisms and casting them into interdisciplinary, multi-physics and multi-scale modelling approaches. Advances in the understanding of chemical reactions, chemo-mechanical interaction, mechanical behaviour, defect evolution, and material degradation, from atomistic scales up to continuum level, are required to resolve many of the most pressing challenges and achieve the goal of material sustainability. These cover every aspect of material life from extraction to production, processing, manufacturing, service life, and recycling. This very recently established group thus focuses on applying and developing computational methods to solve various challenges related to materials and processes with important environmental impact, focusing on problems where the interplay of chemistry, phase transformation, microstructure, mechanics, and damage plays an important role enabling their deformation, mechanical response, and transport properties. Less well known is their influence on material chemistry. The severe lattice distortion at these defects drives solute segregation to them, resulting in strong, localized spatial variations in chemistry that determine microstructure and material behavior. Recent advances in atomic-scale characterization methods have made it possible to quantitatively resolve defect types and segregation chemistry. As shown here for a Pt-Au model alloy, we observe a wide range of defect-specific solute (Au[8, 11, 27, 39, 114, 115].

One example is the simulation of H-based direct reduction of iron ore as an alternative method of steel production with considerably lower emission compared to conventional carbon-based reduction for instance in blast furnaces. Modelling the reduction process by coupled chemo-mechanical phase-field methods including microstructure and defect evolution is an on-going research topic in this group. Close connection to the underlying physics at atomistic scales as well as experimental observation are used in the projects in this group.

Corrosion and damage evolution during the life cycle of metals is one of the most important underlying reason of component failure. Topics such as hydrogen embrittlement, stress corrosion cracking, Li-ion battery degradation are important for clean energy storage (either hydrogen storage or electricity) and are hence also in the focus of projects in this group. The interplay of chemistry, mechanics, and damage development at different scales is important in these topics.

Phase-field, finite element, molecular dynamics, Monte Carlo, and machine learning methods are the computational approaches used by the group. Software packages such as the Düsseldorf Advanced Material Simulation Kit (DAMASK), MOOSE framework, LAMMPS, and TensorFlow are among the tools employed.

Mechanism-based Alloy Design (D. Ponge)

This group works on the microstructure-oriented design of advanced high strength steels, high entropy alloys as well as on engineering Al-, Ni- and Ti-alloys (Fig. 4).

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 [51, 79, 95]. Especially for materials with high strength, hydrogen embrittlement provides a challenge. Here the damage and failure mechanisms are analysed in order to develop novel high strength materials with low susceptibility against hydrogen embrittlement [13, 51, 85, 96, 97]. Projects in the

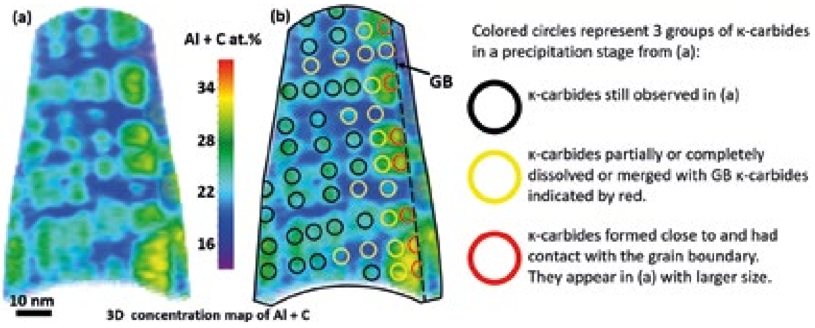

Fig. 4: *Formation and growth of grain boundary (GB) κ-carbides. a) 3D concentration map of Al+C of an APT sample containing a high angle grain boundary (GB) in an Fe-28Mn-8Al-1.3C wt.% alloy aged for 16 h at 550 °C. b) Overlaid image of (a) with a schematic of κ-carbides. κ-carbides formed by spinodal decomposition granting them the periodicity as indicated by coloured circles. The red group benefited from GB diffusion leading to faster growth. Their larger size allows them to consume the yellow group and grow to the sizes observed in (a). These nano-sized GB κ-carbides embrittle the GB in the presence of hydrogen or at low temperatures. During overaging these precipitates grow to micro-sizes and compromise the mechanical properties.*

group make intense use of the processing, mechanical testing, and microstructure characterization facilities at the institute down to the atomic scale. Projects 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 [6, 43, 98]. Depending on phase stability, deformation driven athermal 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.

Microscopy and Diffraction (S. Zaefferer)

This group works on two interconnected tasks: it aims at understanding microstructure formation mechanisms and the relation between microstructures and properties of materials by investigations on the microscopic level. To this aim the group develops or advances novel microscopy and diffraction techniques. Currently the focus lies on techniques in the scanning electron microscope, in particular on the electron diffraction techniques (EBSD, 3D EBSD, XR-EBSD, ECCI) [68, 71, 99–102]. Also, the group has expertise in the field of imaging and diffraction in transmission electron microscopy and X-ray diffraction. With respect to microstructure formation the group pursues questions on deformation, recrystallization, and solid-state phase transformations. Concerning microstructure-related properties the main focus is on mechanical properties, although, in recent years, also corrosion and electronic properties are studied. The spectrum of investigated materials comprises advanced high strength steels of 1st, 2nd, and 3rd generation (dual phase steels, low alloyed TRIP steels, complex phase steels, high-Mn steels, quench and partitioning steels), electrical steels, austenitic stainless steels, superalloys, magnesium-, aluminium- and copper alloys, intermetallic compounds (aluminides, Laves phases), and, since shortly, a range of photovoltaic materials (CdTe, Si, CIGS, GaAs).

Theory and Simulation (F. Roters)

This group develops constitutive models for advanced materials such as high strength steels. As the mechanical properties are of main interest crystal plasticity modelling builds the core of the activities. For this purpose, a number of constitutive models have been developed in the last 15 years. These models cover the full range from phenomenological descriptions to physics-based formulations of dislocation slip and other deformation mechanisms such as twinning induced plasticity (TWIP) and displacive transformations (TRIP). To facilitate the implementation of the models the Düsseldorf Advanced MAterial Simulation Kit (DAMASK, https://damask.mpie.de/) has been developed.

Meanwhile DAMASK was extended to a multi-field solver to enable treatment of multi-physics problems, e.g. thermal effects or damage. The full DAMASK capabilities together with many application examples have been published in an overview paper in 2019 [5]. The extended functionality necessitated a basic refracturing of the code together with a change of the in- and output formats. This work that culminated in the release of DAMASK 3 (see p. 73) was mainly performed in the new ICME group lead by M. Diehl (see p. 39).

One of the key challenges in using complex continuum scale constitutive models is the identification of (unique) parameter sets. To overcome this hurdle a new methodology has been developed to fit these parameters based on macroscopic properties [94]. The same procedures can be used to study parameter interdependencies and sensitivities, which in turn can help to improve the model formulation.

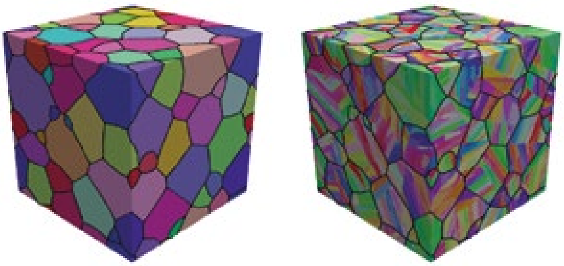

Fig. 5: *Creation of a martensitic representative volume element (RVE); synthetic austenitic microstructure (left) and resulting martensitic microstructure (right). Colours indicate different crystallographic orientations; black lines are grain boundaries.*

Besides reasonable parameter sets, successful microstructure-based simulation of properties relies on high quality representations of those microstructures. To this end a tool has been developed to create representative volume elements for martensite, Fig. 5 [95].

Many industrial processes involve large and heterogenous deformations. Simulation of such processes is challenging as heavily deformed meshes or grids often prevent convergence of the numerical algorithms used. The solution to this problem is remeshing/regridding to create new regular meshes or grids. While this is a standard technique in continuum mechanics, the transfer of microstructural state variables poses additional challenges. Two different strategies have been implemented in DAMASK to enable simulation of large deformations [96].

While all the above sounds rather technical it builds the foundation for the application of DAMASK to complex materials (e.g. bainitic steels) and processes (e.g. hot rolling including dynamic recrystallization) together with our industrial partners and in other groups within the MPIE.

Non-permanent research groups

Most of the more recently esablished non-permanent research groups are presented in separate sections, namely, High Performance Alloys for Extreme Environments (P. Kontis), the ERC-Shine group on Hydrogen in Materials (B. Gault) and Integrated Computational Materials Engineering (M. Diehl) (see p.39).

Two of the non-permanent groups that were founded already before 2019 are the initiatives for High Entropy Alloys (Z. Li) and Materials Science of Mechanical Contacts (M. Herbig).

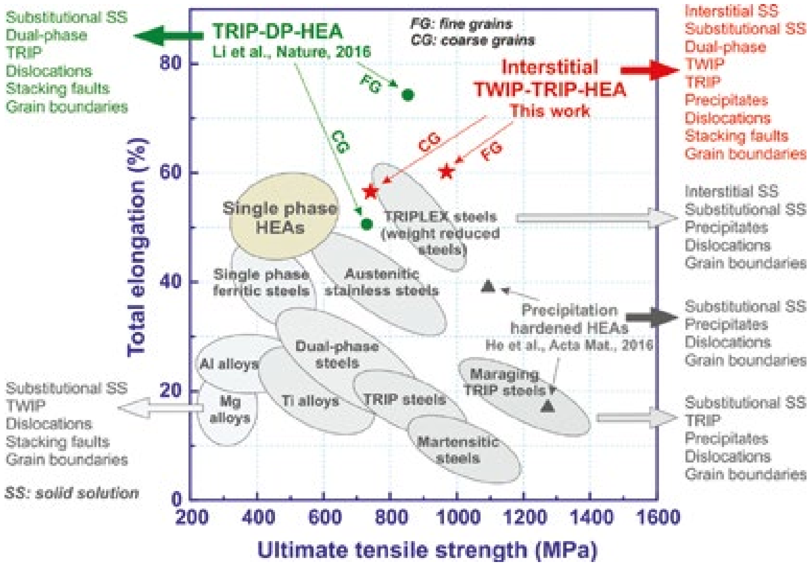

Fig. 6: *Strength-ductility profiles of various classes of metallic materials including novel HEAs recently developed by the group.*

High Entropy Alloys (Z. Li)

The goal of this group is to develop novel high-entropy alloys (HEAs) with exceptional mechanical, physical and chemical properties based on the understanding of their structure-properties relations [21, 91, 106–110]. This is achieved by using advanced experimental techniques and the state-of-the-art theoretical methods, in close collaboration with the other groups and departments.

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 [111, 112].

While conventional alloys use strengthening mechanisms such as grain boundaries, dual-phase structure, dislocation interactions, precipitates, and solid solution (e.g., steels, Ti-alloys, Al-alloys), the novel interstitial TWIP-TRIP-HEAs concept developed by the group combines all available strengthening effects, namely, interstitial and substitutional solid solution, TWIP, TRIP, multiple phases, precipitates, dislocations, stacking faults, and grain boundaries [91, 108, 110, 113, 114]. This leads to the exceptional strength-ductility combination of the novel HEAs, exceeding that of most metallic materials (Fig. 6).

The group conducts projects along a few main topical fields associated with designing high-performance compositionally complex alloys, namely, materials with excellent strength-ductility combination, massive interstitial alloying, alloys with enhanced resistance to hydrogen-embrittlement and corrosion, and multifunctional materials including new alloys combining exceptional mechanical properties with specific magnetic and invar property profiles.

Materials Science of Mechanical Contacts (M. Herbig)

The group aims at deepening our understanding of the materials science phenomena associated with intense joint mechanical and environmental contacts [115–118]. This is key to revealing a broad range of phenomena required for improving crucial engineering components such as bearings, rails, hip implants, extrusion tools, boring heads, cutting inserts, or dental fillings.

The associated materials science of mechanical contacts is versatile and challenging (Fig. 7). The contact between two bodies subjected to high forces under harsh environmental conditions and multiple repetitions involves complex materials science phenomena: plastic deformation can lead to fatigue, grain refinement, and precipitate decomposition. Frictional heat can cause diffusion, phase transformation, recovery, or recrystallization. The presence of air, lubricants, or body fluids at the contact point causes oxidation, tribolayers, or even corrosion or hydrogen embrittlement. These processes usually occur simultaneously in service and cannot be tracked *in situ*. The analysis of such phenomena requires

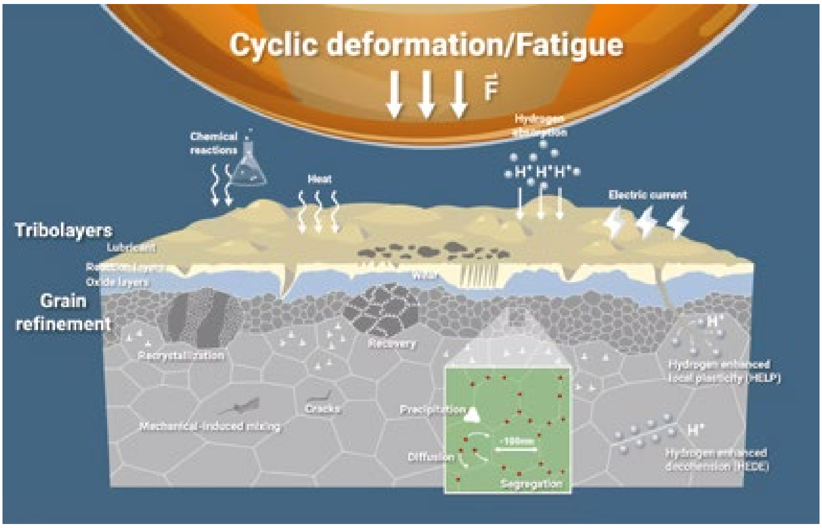

Fig. 7: *Microstructure reactions caused by intense mechanical/environmental contacts..*

combined chemical and structural characterization down to the atomic scale.

One main focus of the group are white-etching-cracks (WECs), which cause failure in bearings and rails, but which are in reality ubiquitous in high carbon steel applications subjected to intense mechanical contacts. This failure mode causes billions of euros costs worldwide each year. The group follows a staggered approach to yield a breakthrough on this long-standing challenge: Specimen failure under controlled laboratory conditions is generated using a customized rolling contact fatigue machine built in-house that simulates test conditions similar to ball bearings but on self-designed alloys. Both, lubrication and loading conditions as well as the electric current flow through the bearing (which is of importance as electric discharge events have been associated with the presence of WECs) can be controlled with this instrument. These specimens are compared to samples that failed during service using state-of-the-art microscopy. Individual phenomena are investigated separately where possible. Dedicated experiments are conducted to investigate the mechanisms of precipitate decomposition by deformation, heat, and electricity.

The research activities on steels are complemented by research on hip implants where corrosion and wear between the stem and head leads to adverse tissue reactions. Here, correlative transmission electron microscopy (TEM) and APT give access to the complex body/implant interactions.

The group uses all characterization techniques available at the MPIE, from rolling contact fatigue test rigs on whole bearings, over mesoscale investigations in the scanning electron microscope (SEM), down to the atomistic scale using TEM and APT. A key competence of the group is the use of correlative probing, for instance by combining these techniques to the same sample, to provide combined 3D structural and compositional information on near atomic scale, which is often the only way to answer a long-standing materials scientific question.

Grand challenges and recent breakthroughs

By bundling the core competences described above the department members jointly pursue a few ‘Grand Challenge’ topics, involving also members from all other departments. Details about some of these projects are given in the section “Interdepartmental Research Activities - Selected Highlights” (see. p. 182 - 225).

The ‘Grand Challenges’ we pursue are

1. Low-dimensional thermodynamics and kinetics at lattice defects
2. Understanding and solving hydrogen embrittlement
3. Compositionally complex alloys with special functional properties
4. Hydrogen-based reduction of iron oxides

Low-dimensional thermodynamics and kinetics at lattice defects

This topic is about the understanding and local chemi-cal manipulation of individual lattice defects. These features, such as dislocations and grain boundaries, influence mechanical, functional, and kinetic proper-ties of alloys. Such changes in the defect’s chemical state can be predicted and experimentally studied under thermodynamic well-controlled grand canonical conditions, for instance by single or multi-component solute decoration. This change in their chemical state leads to changes in energy, mobility, structure, cohe-sion and can even promote local phase transformation. In an approach referred to as ‘segregation engineering’ such solute decoration is not

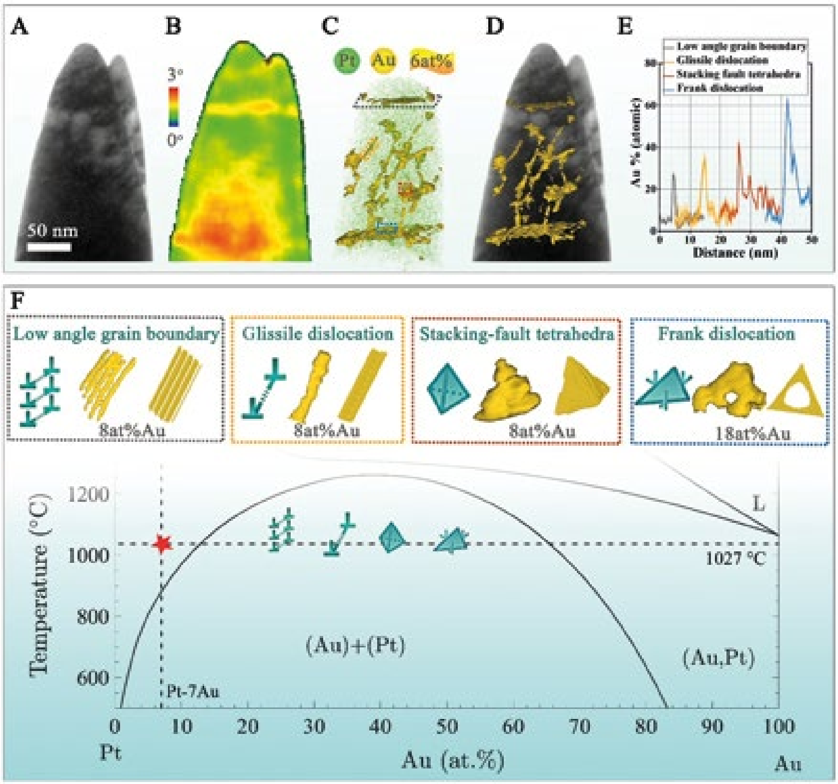

Fig. 8: *Study of a Pt–7 at % Au thin film annealed at 1300 K for 15 min.(A) TEM-based bright-field image of specimen tip oriented normal to the (-1 1 -1) crystallographic direction. (B) Misorientation map from electron diffraction. (C) APT-based reconstruction of the 6 at % segregated Au isosurface superimposed on the bright-field image from (A). The x at % isosurface represents the region (voxels) containing x or more at % Au. (D) Spatial distribution of Pt (green) and Au (gold) atoms in the specimen tip and the isosurfaces from (C). (E) Au at % profiles across particular defects shown in the upper panels in (F). The direction of the profiles in (E) is indicated by the arrows in (F). These include (i) Low-angle grain boundary (grey profile normal to dislocation array), (ii) glissile dislocation (yellow profile parallel to slip plane normal), (iii) stacking fault tetrahedron, and (iv) Frank loop. (F) Top: Each panel shows an image (middle) of each observed defect type, corresponding defect symbols (left), and a DMD simulation result (right) in the coloured boxes. The numbers in each box are the Au at % isosurface (Iso) values for imaging (left) and maximum (max) solute at % near the defects (right). The maximum values are obtained from the Au at % profile in (E). A length of 5 nm is indicated by the bar. Bottom: equilibrium Pt-Au phase diagram [11].*

regarded as an undesired phenomenon but it is instead utilized to manipulate specific defect structures and properties via local composition tuning [57, 119, 137–139].

As an example, for the case of one-dimensional defects we studied the solute decoration of dislocations. Dislocations are one-dimensional defects in crystals, enabling their deformation, mechanical response, and transport properties. Less well-known is their influence on material chemistry. The severe lattice distortion at these defects drives solute segregation to them, resulting in strong, localized spatial variations in chemistry, that determine microstructure and material behaviour. Recent advances in high resolution correlative atomic-scale material characterization have made it possible to quantitatively resolve different dislocation types and arrangements and their respective segregation chemistry. One example for a Pt-Au model alloy is shown in Fig. 8 [11]. We observe here a wide range of defect-specific solute (Au) decoration patterns of much greater variety and complexity than expected from the traditional Cottrell cloud picture. The solute decoration of the dislocations can be up to half an order of magnitude higher than expected from classical theory, and the differences are determined by their structure, mutual alignment, and distortion field. This opens up pathways to utilize dislocations for the compositional and structural nanoscale design of advanced materials. We made similar observations also for Fe-Mn and Al-Mg alloys, revealing by combined atomic-scale characterization and simulation the complexity and diversity of the chemical nature of dislocations.

We studied similar phenomena for the case of grain boundary segregation and found for example complex planar compositional decomposition patterns and even local austenite reversion of these decorated interface regions. In an 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. The grain boundary segregation is a local equilibrium state and shifts the chemical working point from the material's bulk composition to a locally much higher composition. With this shift in the local concentration a number of spatially-confined (hence low-dimensional) thermodynamic phenomena can be observed at lattice defects that do not occur in the adjacent bulk regions.

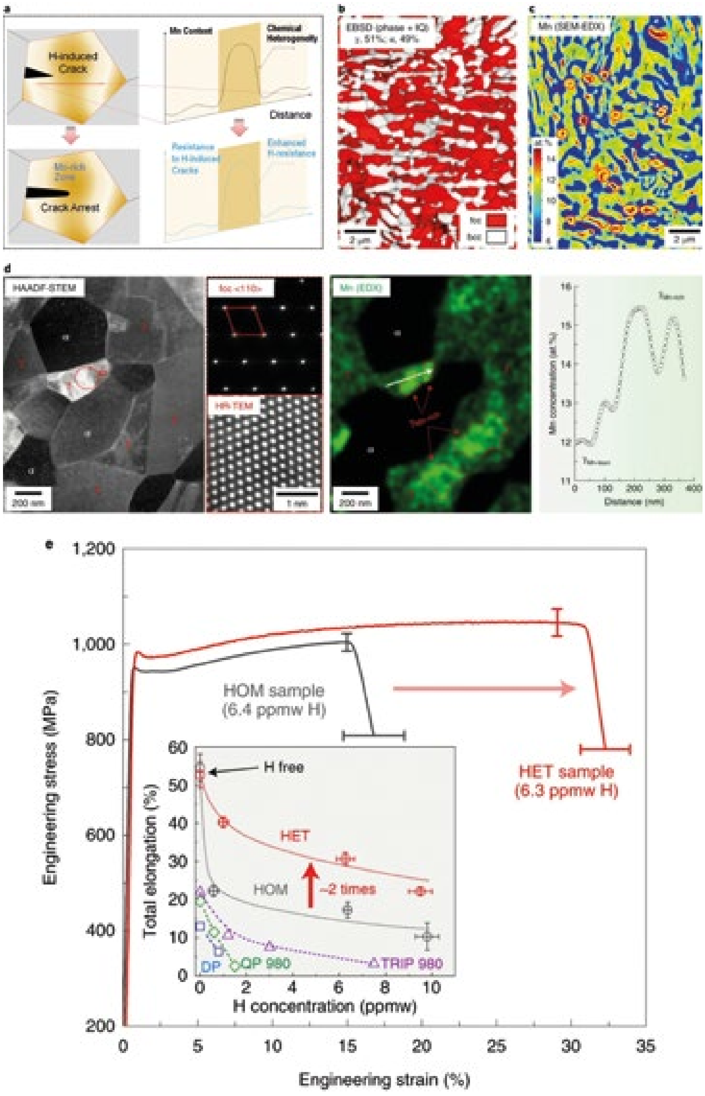

Fig. 9: *a, Schematic image of the concept, showing a H-induced crack propagation crossing a designed solute-rich buffer region, with the solute concentration profile and the corresponding crack resistance schematically shown on the right side. b, Electron backscatter diffraction (EBSD) phase plus image quality (IQ) map showing the austenite–ferrite dual-phase microstructure. fcc, face-centred cubic; bcc, body-centred cubic. c, Scanning electron microscopy (SEM)-based energy-dispersive X-ray spectroscopy (EDX) map revealing the overall Mn distribution pattern in the microstructure. The chemical buffer zones are those regions where Mn is highly enriched (~14–16 at. % Mn) inside the austenite phase (some of them are marked by elliptical frames). d, High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observation with EDX analysis, showing the existence of multiple Mn-rich zones inside one austenite crystal cluster or even one austenite grain. The selected area electron diffraction and high-resolution transmission electron microscopy (HR-TEM) images taken, respectively, from the marked circular and rectangular frames are placed on the right side of the STEM image. The EDX line profile is taken from the area marked by a white arrow in the EDX map. e, Mechanical properties of the chemically homogeneous (HOM) and of the chemically heterogeneous (HET) alloy variant [95].*

Understanding and solving hydrogen embrittlement

One of the main challenges in the field of hydrogen embrittlement is to understand the relationships between the individual hydrogen-induced mechanisms and their synergistic interplay in creating actual damage initiation features that can lead to catastrophic material failure.

Some of the individual effects that hydrogen causes when intruding metallic alloys are in part well-established. An example is the hydrogen enhanced local plasticity (HELP) effect in metals with BCC lattice structure such as ferritic steels. This leads to the local softening of the material due to enhanced mobility of the dislocations. Another effect is the enhanced decohesion across interfaces that can be caused by hydrogen decoration (HEDE). Another important effect is the stabilization of vacancies by hydrogen decoration, leading to super-abundant vacancy concentrations which can condensate and lead to porosity. What is much less understood, however, is how these individual mechanisms actually act together to cause catastrophic damage and failure, Fig. 9 [95].

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 the departments of G. Dehm and M. Rohwerder) in conjunction with EBSD and ECCI as well as nanoscale secondary ion mass spectrometry (nanoSIMS). 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. 50). More details on the latest instrumental progress at the MPIE are presented on pages see p. 50 and p. 204.

These spatially resolved hydrogen mapping methods enabled us not only to establish a relationship between localised plasticity and cohesion effects in steels but also to develop a microstructure design approach that substantially enhances the material's resistance against hydrogen embrittlement. More specific we used our findings to introduce a counterintuitive strategy where we exploit typically undesired chemical heterogeneity within the material's microstructure that enables the local enhancement of crack resistance and local hydrogen trapping (Fig. 9). We deploy this approach to a manganese-containing high-strength steel and produce a high dispersion of manganese-rich zones in the microstructure. These solute-rich buffer regions allow for local micro-tuning of the phase stability, arresting H-induced microcracks thus interrupting the hydrogen-assisted damage percolation. This effect results in a superior hydrogen embrittlement resistance (by a factor of two) without sacrificing the material's strength and ductility. The strategy of exploiting chemical heterogeneities, rather than avoiding them, broadens the horizon for microstructure engineering via advanced thermomechanical processing.

Compositionally complex alloys with special functional properties

An important class of compositionally complex alloys with a wide range of mutual solid solubility has been identified for mixtures of the elements Fe, Ni, Co, Cr and Mn. These elements offer not just interesting opportunities for tuning the stacking fault energy and enhancing the solid solution strength, but they are also known for their strong spin coupling: Fe, Ni and Co are the strongest single element ferromagnets while Cr and Mn are the strongest antiferromagnets. These features, together with a wide range of adjustable valence electron concentrations, has triggered interest in developing alloys with good magnetic and/or invar properties (Fig. 10).

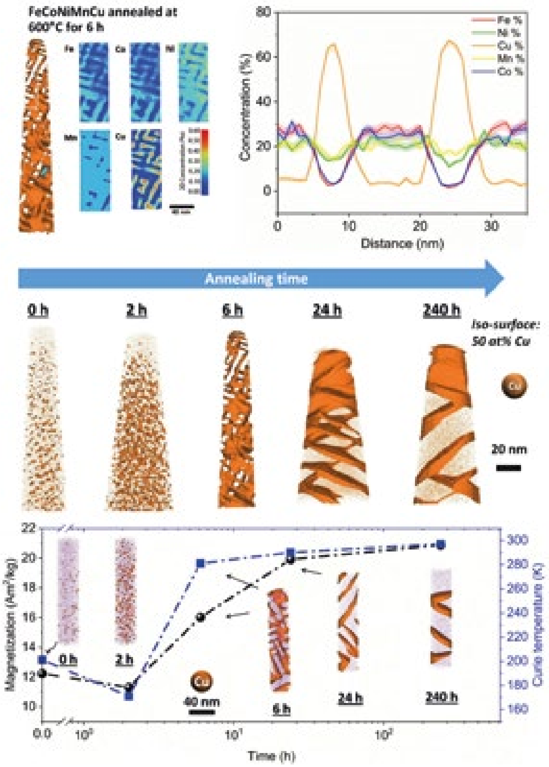

Fig. 10: *APT and magnetic analysis of a homogenized $Fe_{15}Co_{15}Ni_{20}Mn_{20}Cu_{30}$ high entropy alloy annealed at 600 °C for several times. APT tip reconstructions of Fe, Ni, Co, Mn, and Cu. 50 at. % iso-concentration surfaces of Cu and in-plane compositional analysis of the identical sample region marked on the isoconcentration surfaces [89, 106].*

One project in that context targets mechanically strong soft-magnetic alloys. The motivation behind that is that a lack of strength and damage tolerance can limit the applications of conventional soft magnetic materials, particularly in mechanically loaded functional devices which are critical for the electrification of transport and industry. Therefore, strengthening of these materials is important. However, conventional strengthening concepts usually significantly deteriorate soft magnetic properties, due to Bloch wall interactions with the defects used for hardening. We followed therefore a novel concept to overcome this dilemma, by developing bulk alloys with excellent mechanical and attractive soft magnetic properties through coherent and ordered nanoprecipitates (<15 nm) dispersed homogeneously within a face-centred cubic matrix of a non-equiatomic CoFeNiTaAl high-entropy alloy (HEA) [54]. Compared to the alloy in precipitate-free state, the alloy variant with a large volume fraction (>42 %) of nanoprecipitates achieves significantly enhanced strength (≈1526 MPa) at good ductility (≈15 %), while the coercivity is only marginally increased (<10.7 Oe). The ordered nanoprecipitates and the resulting dynamic microband refinement in the matrix significantly strengthen the HEAs, while full coherency between the nanoprecipitates and the matrix leads at the same time to the desired insignificant pinning of the magnetic domain walls.

Another approach made use of tailoring magnetic properties via spinodal decomposition in compositionally complex alloys, Fig. 10 [89, 106]. While the original version of the high-entropy alloy concept aimed at stabilizing single- or dual-phase multi-element solid solutions through high mixing entropy, we modified this strategy by rendering such massive solid solutions metastable, to trigger spinodal decomposition for improving the alloys' magnetic properties. The motivation for starting from a complex composition for this approach is to provide the chemical degrees of freedom required to tailor spinodal behaviour using multiple components. The key idea is to form Fe-Co enriched regions which have an expanded volume (relative to unconstrained Fe-Co), due to coherency constraints imposed by the surrounding HEA matrix. As demonstrated by theory and experiments, this leads to improved magnetic properties of the decomposed alloy relative to the original solid solution matrix. In a prototype magnetic FeCoNiMnCu HEA, we could show that the modulated structures, achieved by spinodal decomposition, lead to an increase of the Curie temperature by 48 % and a simultaneous increase of magnetization by 70 % at ambient temperature as compared to the homogenized single-phase reference alloy. The findings thus open a pathway for the development of advanced functional compositionally complex alloys.

Hydrogen-based reduction of iron oxides

Steel is the most important material class in terms of volume and environmental impact. While it is a sustainability enabler, for instance through lightweight design, magnetic devices, and efficient turbines, its primary production is not. Iron is reduced from ores by carbon, causing 30 % of the global CO_2 emissions in manufacturing, qualifying it as the largest single industrial greenhouse gas emission source. Hydrogen is thus attractive as alternative reductant. Although this reaction has been studied for decades, its kinetics is not well understood, particularly during the wüstite reduction step which is much slower than hematite reduction.

Some rate-limiting factors of this reaction are determined by the microstructure and local chemistry of the ores. Here, we report on a multi-scale structure and composition analysis of iron reduced from hematite with pure H_2, reaching down to near-atomic scale. During reduction a complex pore- and microstructure evolves, due to oxygen loss and non-volume conserving phase transformations. The microstructure after reduction is an aggregate of nearly pure iron crystals, containing inherited and acquired pores and cracks. We observe several types of lattice defects that accelerate mass transport as well as several chemical impurities (Na, Mg, Ti, V) within the Fe in the form of oxide islands that were not reduced. With this work, we aim to open the perspective in the field of carbon-neutral iron H-based direct reduction from macroscopic processing towards better understanding of the underlying microscopic transport and reduction mechanisms and kinetics [27].

Reduction based on a hydrogen plasma may offer an attractive alternative to direct reduction. We therefore also study the reduction of hematite using hydrogen plasma. The evolution of both, chemical composition and phase transformations was investigated in several intermediate states. We found that hematite reduction kinetics depends on the balance between the initial input mass and the arc power. For an optimized input mass-arc power ratio, complete reduction was obtained within 15 min of exposure to the hydrogen plasma. In such a process, the wüstite reduction is also the rate-limiting step for complete reduction. Nonetheless, the reduction reaction is exothermic, and its rates are comparable with those found in hydrogen-based direct reduction. Micro- and nanoscale chemical and microstructure analysis revealed that the gangue elements partition to the remaining oxide regions, probed by energy dispersive spectroscopy (EDS) and APT. Si-enrichment was observed in the interdendritic fayalite domains, at the wüstite/iron hetero-interfaces and in the primarily solidified oxide particles inside the iron. With proceeding reduction, however, such elements are gradually removed from the samples so that the final iron product is nearly free of gangue-related impurities. Our findings provide microstructural and atomic-scale insights into the composition and phase transformations occurring during iron ore reduction by hydrogen plasma, propelling better understanding of the underlying thermodynamics and kinetic barriers of this essential process [28].

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Department of
Structure and Nano-/Micromechanics of Materials (SN)

G. Dehm

Scientific mission and concepts

Mission

We perform basic research interlinking mechanical, and since 2019, the electrical properties of materials with their microstructure and constitution. Establishing such links requires multiscale approaches in materials characterization and property measurement. The gained information provides a strong basis for designing optimized material microstructures and systems with respect to improved lifetime in harsh environments, reduced energy consumption in transportation or higher efficiency in energy applications. While obtaining global properties is often well established, accessing properties that emerge at small dimensions from ca. 100 micrometres down to a few nanometres requires novel test strategies and protocols. We place our focus on adapting and developing reliable miniaturized experiments to obtain precise information on mechanical and electrical properties at these small length scales [1-7]. The high spatial resolution of our nanoindentation and 4-point probe based mechanical and electrical experiments, respectively, provide us access to the properties of individual phases in multiphase materials, which are often so far unexplored. Even more challenging are the complex interactions between different classes of imperfections such as between dislocation and grain boundaries [9-11] or dislocations and point defects [12-15], which is another focus of our work. As materials are always exposed to certain environmental conditions in applications, we have recently extended our small scale mechanical experimental portfolio to low (-150 °C) and elevated temperatures (800 °C), to variable strain rates (10^{-4} s^{-1} - 10^{4} s^{-1}) and also to hydrogen exposure – the latter in the new ERC funded group Hydrogen Mechanics and Interfaces (J. Duarte Correa). Combining our small-scale mechanical tools with advanced electron microscopy techniques and X-ray diffraction/synchrotron radiation methods allow us to control boundary conditions and to elucidate underlying deformation mechanisms. Similarly, *in situ* electrical characterization permits us to study site specific various families of defects down to a single coincidence site lattice grain boundary [16]. Understanding defects requires knowledge of their crystallography, chemical composition, bonding, and atomic structure. We use advanced scanning transmission electron microscopy (STEM) techniques, correlative electron microscopy and atom probe tomography (APT, often in collaboration with the MA department) to obtain this information [17-28]. Image simulations, machine learning, and atomistic simulations often in close collaboration with the CM department complemented by our new ERC funded group Atomistic Modelling of Material Interfaces (T. Brink) guide us with the necessary data interpretation [11, 13, 23, 26, 27, 29-31].

Our materials portfolio stretches from intermetallic materials [32-49] to chemically complex alloys / high entropy alloys (CCA/HEA) [12, 21, 50-56] and thin films [4, 25, 29, 52, 57-69] with specific aims. For example, next generation titanium aluminides for aero-engines target at extreme reductions in CO_2 and NO_x emission, while iron aluminides show great potential as an easy-to-recycle material for stationary engines and critical components in wind turbines. Our research often begins with establishing ternary phase diagrams, as literature lacks the requisite accurate data, critical for obtaining specific phases and microstructures. For CCA/HEA, we aim at improving high temperature strength by tailoring the microstructure towards those of superalloys and elucidate their resistance against hydrogen in the near future. An alternative approach to prevent hydrogen embrittlement of alloys is impeding hydrogen ingress by applying diffusion barrier coatings. This route we examine in a consortium with the independent research group Nanoanalytics and Interfaces (C. Scheu) at the MPIE. We test the impact of hydrogen on mechanical properties as well as its impact on nanostructure. In addition, we also elaborate on model materials, such as macroscopic bi-crystals with the help of the MPIE's central synthesis facility or elemental metal films fabricated in-house by SN department in a deposition cluster [10, 25, 59, 70, 71]. Those model materials are employed for very specific microstructure-property aspects, like the question if phase transformations of grain boundaries exist in pure elemental systems and how alloying additions would influence the transformation [19, 22, 23, 27, 28].

Department structure and laboratories

The department currently consists of 7 research groups closely interacting on our department's mission. The research groups Intermetallic Materials (M. Palm and F. Stein) and Thin Films & Nanostructured Materials (M. Ghidelli until Jan. 2020, J. Best since April 2020) are central to our and the institute's materials portfolio. They operate a modern thermodynamic laboratory, and thin film deposition facilities (with GO department), respectively. The 2013 established group Nano-/ Micromechanics of Materials (C. Kirchlechner until Dec. 2019, J. Best since April 2020) is complemented by the two new groups Hydrogen Mechanics and Interfaces (J. Duarte Correa, since 2019) and Nanomechanical Instrumentation and Extreme Nanomechanics (R. Ramachandramoorthy, since July 2020). This puts us now in a unique position for small-scale testing under hydrogen exposure with an in-house developed electro-chemical cell for back-side charging [7] (see p. 66), and developing new instrumentation for an expanded temperature and strain rates (≤10^4 s^{-1}) regime and variable gas environments (see p. 56). The group Advanced Transmission Electron Microscopy (C. Liebscher) hosts our aberration corrected TEM/STEM instruments (one probe corrected, one image corrected) as well as two conventional TEMs and specimen preparation facilities for conventional techniques and focussed ion beam (FIB) methods. One major scientific objective revolves around the ERC Advanced Grant GB-Correlate (G. Dehm) aiming at resolving and understanding grain boundary phase transitions in pure and alloyed metals. This task is now supported by the recently established group Atomistic Modelling of Material Interfaces (T. Brink, since 01/2020) financed by the ERC Advanced Grant, which also supports the group Hydrogen Mechanics and Interfaces (J. Duarte Correa, since 09/2019). This group performs atom probe tomography (APT) measurements on the chemical composition at grain boundaries and maps hydrogen in materials; the latter often in cooperation with the MA department. The activities of the former research group Nanotribology (S. Brinckmann until 12/2019) is now integrated in the group Nano-/ Micromechanics of Materials. S. Brinckmann, who accepted a tenured position at Research Centre Jülich, still co-supervises ongoing activities.

the AvH postdoc Y. Yao is now full professor at Xi'an (Northwestern Polytechnical University). Several postdocs became assistant or associate professor in China (W. Guo, W. Xia, W. Lu) and India (M. Kini, A. Kumar Saxena). We also have a large share of former postdocs and PhD students entering industry (e.g. steel industry, electronics industry, and companies for scientific instrumentation).

We support our department members' career development by personal interview trainings, offering external soft skill courses and a dedicated MPIE mentoring program (see p. 99) for selected female postdoc & staff scientists.

The high quality of our team members' research is also well documented by several awards. Examples for our PhD students are the selection for participation in the Lindau Nobel Laureate Meeting 2019 (N. Peter), the travel award of the Wilhelm und Else Heraeus Foundation (L. Frommeyer, 2020), and a Best Poster Award for S. Ahmet for her excellent work on grain boundaries in aluminium at the multinational microscopy conference MC2021. Z. Kahrobaee and M. Palm received the Editor´s Choice Award of the Journal of Phase Equilibria and Diffusion for their paper "Critical Assessment of the Al-Ti-Zr System" [42]. Last but not least the ERC Advanced Grant GB-CORRELATE (G. Dehm) (see p. 49), for which the sole selection criterion is excellence, was granted in 2018 and finances with 2.5 Mio€ for 5 years a large portion of the department's research work on grain boundary phase transitions.

Fig. 1: *The SN department and independent research group Nanoanalytics & Interfaces at the joint 2020 retreat in Lingen. Photo A. Frank.*

Personal development, careers and awards

Changes in our department's research groups are strongly linked to the excellent career opportunities of our scientists. C. Kirchlechner was appointed as tenured full professor and institute director at Karlsruhe Institute of Technology (KIT), S. Brinckmann became a permanent group leader at the Research Centre Jülich, and M. Ghidelli obtained a permanent staff scientist position at CNRS (Sorbonne, France). All three remain involved in co-supervision of PhD students who started under their guidance at SN department. Two former Alexander von Humboldt (AvH) awarded postdocs, S. Lee and X. Fang became group leaders at KIT and TU Darmstadt, while

Our international department members are often supported by prestigious fellowships from different countries and societies. In Germany, best known is the Alexander von Humboldt foundation, where excellent researchers are granted 1 to 2 year-long research stays in Germany. In 2020, D. Chatain, from CINAM – Centre Interdisciplinaire de Nanoscience de Marseille (France) received the Humboldt Research Award for established faculties and Y. Zhu from North Carolina State University (USA) the Friedrich Wilhelm Bessel Research Award for emerging faculties. Furthermore, Alexander von Humboldt Postdoc Fellowships were awarded to X. Fang, S. Lee, Y. Yao, X. Zhou (jointly with MA department), D. Xie, N. Cheng (jointly with Nanoanalytics & Interfaces), and Carvalho Silva.

Third party research projects

The SN department is actively integrated in several German Science Foundation (DFG) funded collaborative research centers, which align with the department's research mission. We are partners of: SPP 2006 Compositionally Complex Alloys - High Entropy Alloys (CCA - HEA), SPP 1594 Topological Engineering of Ultra-Strong Glasses (ended 2020), TRR188 Damage Controlled Forming Processes, and the SFB 1394 Structural and Chemical Atomic Complexity: From Defect Phase Diagrams to Material Properties (started 2020). Within the topic of HEA/CCA we also had until 12/2020 a joint French-German project on the stability of high entropy alloys (HEA) thin films with partners in Marseille (CNRS), Antipolis (U Mines Tech), and Bochum (RUB). Part of our hydrogen activities are funded in a joint project with the Leibniz Institute in Greifswald, Helmholtz Center HEREON in Geesthacht, and the independent research group of C. Scheu at the MPIE. Within the European Union's Horizon 2020 research and innovation programme the department is involved in the project ADVANCE, which is part of the Clean Sky 2 joint undertaking (see p. 88). Since 2021, we are part of the new Eurostars project – HINT. The ERC Advanced Grant GB-CORRELATE drives to a large extend our research on phase transformations of grain boundaries and their impact on material properties (see p. 49). Furthermore, we perform basic research projects with international scientific and European industrial partners. These projects are typically funded by the corresponding national state authorities such as the ministry of science or economics. Within the Max Planck Society we are connected to several institutes in the Max Planck PhD school Surmat and the Big Max activity on Big-Data-Driven Materials Science (see p. 82). The SN department also hosts 2 international Max Planck Partner groups led by excellent previous department members. The group *Designing Damage Tolerant Functional Oxide Nanostructures* (head: N. Jaya Balila, see p. 32) aims at improving the fracture resistance of brittle materials by incorporating interfaces. The external research group *Microstructure Design of High-performance Materials for Harsh Energy Applications* (head: J. Zavašnik, see p. 35) explores interactions of light elements (hydrogen, helium) with materials required for the hydrogen economy and fusion reactors, respectively.

Community service and teaching

The department supports the community by multiple reviewing and evaluation activities, serving in scientific and scholarly committees, participating as lecturers in conferences and schools, and by (co-)organizing workshops and conferences. The most prominent examples for conference (co-)organization are: "International Workshop on Advanced In Situ Microscopies of Functional Nanomaterials and Devices – IAMNano 2019" (G. Dehm, C. Liebscher, C. Scheu, B. Völker), "International Workshop on Laves Phases" (F. Stein 2019), "High entropy and compositionally complex alloys" (C. Liebscher, DPG 2019), Metals, Alloys and Intermetallics at the Microscopy Conference MC2019 (G. Dehm), "4th and 5th MSIT Winter School on Materials Chemistry" (M. Palm, F. Stein, 2020, 2021), "Nanobrücken 2020: A Nanomechanical Testing Conference" (G. Dehm, C. Kirchlechner, 2020), "TOFA 2020 – International Conference on Thermodynamics of Alloys" (F. Stein, M. Palm), "BiGmax Workshop 2020 on Big-Data-Driven Materials Science" (C. Liebscher with CM, and MA, 2020) and "BiGmax summer school „Harnessing big data in materials science from theory to experiment" (C. Liebscher with CM, 2021), "Intermetallics 2019 and 2021" (M. Palm, F. Stein), "International Conference on Metallurgical Coatings and Thin Films – ICMCTF" (J. Duarte, 2020, 2021), MRS Symposium "In Situ Mechanical Testing of Materials at Small Length Scales, Modeling and Data Analysis" (G. Dehm 2021).

Our close link to the nearby universities in Bochum (RUB) and Düsseldorf (HHU) is manifested in teaching courses on advanced TEM (G. Dehm, C. Liebscher), small-scale mechanical testing (G. Dehm supported by several group leaders and postdocs), and atomic resolved characterization (G. Dehm, C. Scheu), which can be also attended by our PhD students and postdocs. During the Corona pandemic, all lectures were given online. In addition, we make annual retreats with external guest scientists (except 2020 due to COV19), hold invited talks and discussion meetings with external scientists, and have a lively weekly joint SN and NG seminar series in addition to smaller group meetings. Since spring 2020, these seminars are all online.

The SN department is very well connected within the MPIE as seen by several multi-author papers where different techniques of the departments are connected, as for hydrogen related topics APT (MA), *ab initio* simulations (CM), Kelvin probe microscopy (GO), together with our TEM and small-scale testing capabilities.

The next chapter summarizes our main scientific breakthroughs followed by a more focused report on the scientific achievements of the research groups of the SN-department.

Main scientific breakthroughs

We have gained new insight in the existence of grain boundary (GB) phases in elemental metals and alloys by using thin films as model systems. Prominent examples are our Cu and Al films grown on (0001) α-Al_2O_3 substrates serving as ideal template systems due to their strong (111) texture with a large number of connected tilt grain boundaries ranging from low angle to high angle coincidence site lattice (CSL) GB. The strong (111) texture permits to resolve the atomic grain boundary structure by STEM/TEM with subatomic precision for a variety of GBs. Complementary molecular dynamic (MD) simulations are used to verify/predict stable grain boundary phases. We observed for the first time experimentally the coexistence of two different atomic motifs for Cu for a ∑19b grain boundary [23]. Very similar motifs exist also for the ∑37 grain boundary in Cu [27]. MD simulations confirm the observed grain boundary phases to possess different excess properties (volume, stress) and different stability ranges depending on temperature and stress. This shows that even in elemental metals grain boundary phase transitions occur more frequently than originally assumed! In order to tackle their influence on material properties, in 2019 we initiated high-resolution electrical measurements performed at room temperature. To obtain the resistivity of single grain boundaries we had to develop a novel approach with high position accuracy and so far unreached electrical sensitivity [1]. With this new tool we managed to detect a clear correlation between grain boundary excess volume and grain boundary resistivity for different CSL type grain boundaries in Cu [16]. Along the same lines, our micromechanical experiments on twin boundaries in Cu and Ag accompanied by MD simulations with the CM department reveal that a breakthrough stress for transmissible dislocations is in the range of shear stresses required for cross-slip [9-11, 64]. However, the maximum length of the mobile dislocation segment controls the required stress for dislocation motion rather than the “breakthrough stress” of the twin boundary [9, 10, 64]. Confining the dislocation by multiple finely spaced twins significantly contributes to the stress increase of nanotwinned materials [10].

Interaction of dislocations with lattice defects has been advanced by our studies on FeCoCr(Mn)Ni HEA and hydrogen charged Fe-Cr alloys. The jerky dislocation motion observed by *in situ* TEM straining experiments in the FeCoCr(Mn)Ni HEA [12, 13], does not require short range order. We could exclude short range order experimentally by advanced STEM, STEM-EDS and APT within the resolution limits [12]. MD simulations revealed that even with random atomic arrangements local fluctuations in the Peierls stress exert pinning points of different strength for dislocations [13]. In this collaboration within the SPP 2006 HEA/CEA with the TU Darmstadt we observed that strongest pinning points arise if Co atoms possess a Cr rich atomic neighbourhood within the random lattice occupation [13].

Hydrogen as a future energy source requires a fundamental understanding of hydrogen embrittlement processes. This we address by localized nanomechanical testing [7, 14, 15]. Currently single grains with different orientations in bcc Fe-Cr steels are in our primary focus. We found that the easier dislocation nucleation with diffusible hydrogen leads to an increase in dislocation density and thus a hardness increase compared to hydrogen-free Fe-Cr. The results are in accordance with the defectant theory predicting a reduction in dislocation line energy under hydrogen. In contrast to other studies in literature, we could prove that the Young’s modulus remains unaffected by the hydrogen ingress. This was only possible due to our novel back-side charging electrochemical cell developed in-house [7].

We made also progress in tuning the microstructure for improved high temperature materials required for CO_2 reduced transportation and energy generation. Novel superalloys based on the HEA system with the base elements AlFeNiTi where accomplished with creep resistance similar to commercial Ni-base superalloys [53, 54, 72]. For Ti-Al and Fe-Al based materials several highly accurate ternary phase diagrams have been developed in the last years [38, 42, 73-78]. While this is only a selection of most prominent examples, further details and examples are listed in the next sections under the individual research groups.

Scientific groups

Advanced Transmission Electron Microscopy (C. Liebscher)

Group mission

The mission of this group is to advance modern techniques in the transmission electron microscope (TEM) to unravel the micro- and nanostructural origins responsible for the functionalization of materials. We develop novel 4D-scanning TEM (STEM) techniques to explore grain and phase orientations in nanostructured alloys [30, 43], advance *in situ* techniques to observe the dynamic evolution of complex alloys under an applied strain [12, 79] or temperature [21, 80] and novel data analysis algorithms for improving atomic resolution imaging and automating its analysis [81, 82]. We apply the techniques to discover novel phenomena at grain boundaries down to atomic resolution [22, 23, 26, 28, 83], design new alloys with superior mechanical properties [20, 50, 53-55, 71, 84, 85] and push the boundaries in big data driven microscopy. Our goal is to understand the fundamental physical mechanisms active in materials and alloys at the atomistic level, building the foundation for the design of materials with superior functional [80, 86] and mechanical properties.

Grain boundary phase transformations

This is the biggest research topic within this group and covers many aspects across different material systems [22, 23, 26, 28, 59, 83]. The notion that grain boundaries, the interfaces separating individual crystals in a polycrystalline material, can exist in multiple phase states was established by thermodynamic concepts already more than 50 years ago. However, it was not possible to observe them at atomic resolution since grain boundaries are essentially confined, two-dimensional defects with a width of only a few atomic distances – buried in the material. Furthermore, they can adopt complex topographies [87] and only little is known about the discrete arrangement of atoms as well as solute species. We combine the synthesis of defined grain boundary geometries, site-specific sample preparation, atomic resolution characterization and atomistic modelling to discover the underlying nature of grain boundary phase transformations in metallic alloys.

It was so far only possible to explore grain boundary phase transformations in elemental metal systems by computer simulations. Together with T. Frolov (LLNL, USA), who is a world leading expert in atomistic modelling of grain boundary phases, we developed a direct correlation of atomic scale experimental observations and simulations of grain boundaries to explore novel interface phenomena. We could show experimentally for the first time that two grain boundary phases can occur at symmetric and asymmetric $\Sigma 19b(178)[11\bar{1}]$ tilt grain boundaries in an elemental Cu thin film [23]. As shown in the atomic resolution high angle annular dark-field (HAADF) STEM image of Fig. 2, the grain boundary structure transforms abruptly from the pearl phase (blue) to the domino phase (red). The same structures were found by grain boundary structure prediction based on an evolutionary algorithm and their difference in thermodynamic excess properties suggested that the two-phase pattern observed in experiment emerged from a first order transformation. By finite temperature MD simulations, we could establish that stresses are needed to stabilize the metastable domino phase. However, this could not explain the room temperature observations in experiment. The key to the answer of this question was the existence of a new, so far overlooked line defect, the grain boundary phase junction, which separates the two grain boundary phases (Fig. 2b). Temperature dependent MD simulations revealed that the migration of the phase junction is strongly temperature dependent and it is made responsible for kinetically trapping the transforming grain boundary phases for temperatures below ~500 K, which is ~200 K below the annealing temperature of the Cu thin film [23]. We are currently extending these observations to $\Sigma 37c\ [11\bar{1}]$ tilt grain boundaries in Cu, where we even witness a nanoscale dual-phase patterning of the grain boundary by similar grain boundary phases [27] (see section *Atomistic Modelling of Material Interfaces*, T. Brink). These observations require a paradigm-shift on how we treat grain boundaries and may open novel pathways to use the phase behaviour of interfaces to sculpt advantageous microstructures.

In related work, we have performed controlled segregation studies of similar $\Sigma 19b[11\bar{1}]$ tilt grain boundaries by doping them with Ta and Zr [22]. In the case of Ta, small nanosized Ta-particles are observed to form at the grain boundaries, which seem to pin them against movement during the annealing treatment. We could not observe any sign of Ta segregation to the grain boundary. This is different for Zr, where strong anomalous segregation is revealed. Our atomic resolution observations coupled to energy dispersive X-ray spectroscopy showed that Zr seems to disrupt the regular grain boundary structure in a $\Sigma 19b(178)[11\bar{1}]$ boundary, forming a glass-like grain boundary phase. A different behaviour was found for a faceted grain boundary, were Zr preferentially segregates into the facet junctions and disorders their core structure. These segregation-induced grain boundary transformations open a plethora of possibilities to further tune interface properties to tailor grain boundary mobility or the transport properties of interfaces.

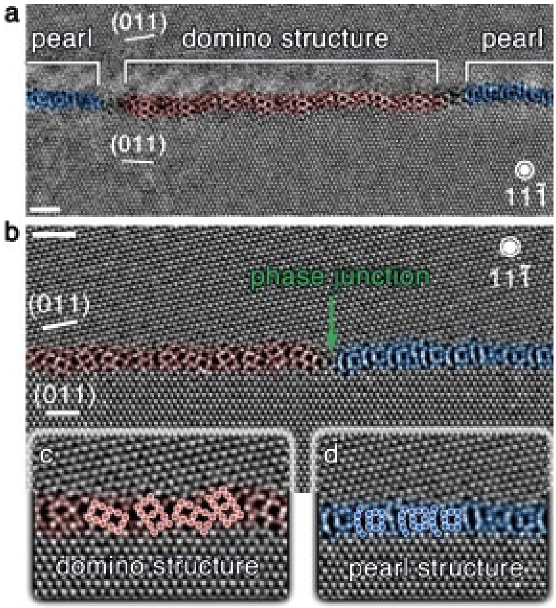

Fig. 2: *Atomic resolution HAADF-STEM images of two grain boundary phases pearl (blue) and domino (red) at an a) symmetric and b) asymmetric grain boundary in Cu. b) highlights the location of the grain boundary phase junction. c) and d) show details of the structural units of both grain boundary phases (from [23]).*

The segregation studies were extended to explore effects on asymmetric grain boundaries, which are rarely studied experimentally. We found that Ag segregation induces a nanofaceting transition at an asymmetric near $\Sigma 5(310)$ [001] tilt grain boundary in Cu [28, 83]. Atomic resolution STEM observations showed that the initial Ag-free grain boundary is asymmetric and adopts a rather complex structure. However, no facet formation was observed even after long term annealing at 800 °C for 120 h. The Ag-segregated boundary, which was annealed under similar conditions, showed distinct symmetric (210) facets that contained most of the Ag solutes. These facets, which were on the order of only several nm in size, adopted a kite-type structural unit, where the Ag atoms occupied the kite-tips and nearly filled an entire atomic column, as determined by STEM image simulations [28, 83]. The symmetric Ag-rich facets were separated by nmsized Ag-lean asymmetric facets. In combination with MD simulations performed by T. Frolov (LLNL, USA), we could establish that Ag promotes the nucleation of the symmetric facets since the observed kite-structure is the lowest energy configuration. In recent work, we found that the facet evolution is strongly dependent on the Ag concentration by designing a diffusion couple geometry, where Ag diffusion was perpendicular to the tilt axis [28]. At low Ag concentration, the grain boundary remains flat and asymmetric and with increasing local Ag content, the emerging symmetric Ag-rich facets grow from several nm to tens of nm until a fully symmetric (210) segment emerges close to the Ag reservoir.

Compositionally complex alloys

The emergence of high entropy alloys (HEA), where five or more elements are mixed at near equal concentration, offers new opportunities for alloy design. We have employed our advanced characterization techniques to discover the fundamental deformation mechanisms in metastable, dual-phase $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ (at.%) alloys with unmatched work hardening ability. Atomic resolution STEM imaging revealed that both the pre-existing face-centred cubic (fcc, γ) and hexagonal close packed (hcp, ε) domains in an as-processed alloy are composed of a nanolaminated structure, where hcp-nanolaminates form in fcc and vice versa [21, 79]. *In situ* straining in the STEM lead to the observation that the microstructure undergoes a dynamic forward transformation from $\gamma \rightarrow \varepsilon$ and backward from $\varepsilon \rightarrow \gamma$ upon straining, which we termed a bi-directional transformation induced plasticity effect. Ultimately, this leads to a hierarchical nanolaminated structure during deformation, which explains the excellent combination of strength and ductility of the alloys.

An extension of the outstanding room temperature mechanical properties was achieved in a similar alloy system of composition $Fe_{19.84}Mn_{19.84}Co_{19.84}Cr_{19.84}Ni_{19.84}C_{0.8}$ (at.%) by interstitial alloying with C [21]. We could show that nanotwinned regions in this alloy can be stabilized even to elevated temperatures of 700 °C by the formation of elongated $Cr_{23}C_6$-type nano-carbides. Atomic resolution STEM observations, STEM-EDS and *in situ* heating in the STEM reveal the underlying formation mechanisms of the nano-carbides. During annealing at 800 °C or 900 °C after cold rolling, the coherent twins in the nanotwinned regions undergo de-twinning forming nanosized incoherent twin boundary segments consisting of a dense dislocation network. Through thermal activation 9R phases are observed to nucleate at these incoherent segments, where the phase boundaries of the 9R phase ultimately serves as nucleation site of the nano-carbides. They in turn prevent further de-twinning and pin the twin boundaries from migrating, stabilizing the nanotwinned regions up to temperatures of 800 °C.

To advance the development of light weight, high temperature alloys, we have designed novel alloys in the composition space Al-Cr-Fe-Ni-Ti within the DFG priority program 2006 in collaboration with J. Schneider (RWTH Aachen University), U. Glatzel (University of Bayreuth) and the Intermetallics group (M. Palm, F. Stein). By combinatorial thin film screening we could efficiently identify suitable alloy candidates in the vast, unexplored composition space being comprised of a disordered bcc (A2) matrix and B2 and/or $L2_1$-type ordered precipitates [53, 54, 66]. Through compositional refinement and microstructural design we developed a low density alloy with composition $Al_{20}Cr_{20}Fe_{35}Ni_{20}Ti_5$ (at.%) and nominal density of 6.4 g/cm^3 with a yield strength of ~200 MPa at 900 °C and excellent creep properties at 800 °C [53].

The key to understand the mechanical properties in these highly concentrated solid solutions of HEAs is to observe

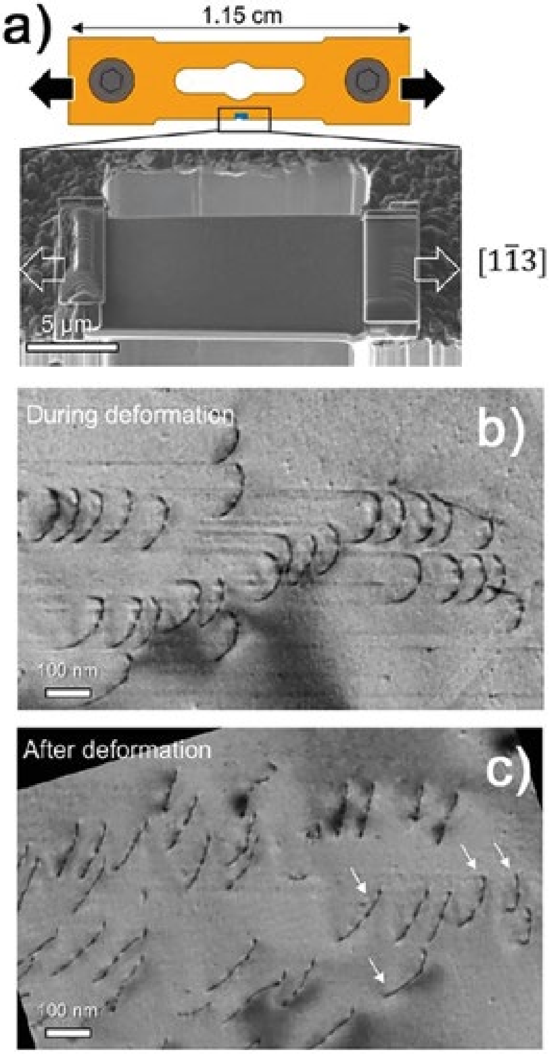

Fig. 3: *a) Custom built in situ straining inset and FIB prepared HEA sample prior to straining. b) Bowed dislocations during deformation. c) Partially bowed dislocations after straining indicated by arrows.*

how dislocations move through the lattice. We have developed a strategy to determine the size dependent micromechanical properties by *in situ* pillar compression in the scanning electron microscope (SEM) [88] and TEM [12] and correlated the mechanical properties to direct observations of dislocation glide by *in situ* straining in the TEM. We found a smaller size scaling exponent for a single crystal nominally equimolar FeMnCoCrNi alloy in comparison to other fcc metals reported in literature suggesting that solid solution hardening or a high lattice friction stress are dominant mechanisms. The direct observation of jerky dislocation motion and quantification of fluctuating local stresses acting on the dislocations (Fig. 3) lead to the conclusion that pinning sites are active. No traces of a local chemical short-range ordering was found by atomic scale STEM and APT characterization. An atomistic study performed in collaboration with the TU Darmstadt (K. Albe, D. Utt) revealed that local changes in the Peierls stress can already explain the jerky dislocation motion [13].

Big data and machine learning

With the advent of high-speed electron detectors new imaging modalities in the STEM emerged that enable to capture local crystallographic information with high spatial resolution. These 4D-STEM techniques, where in each probe position a full electron diffraction pattern is recorded, require also the development of new data treatment and analysis schemes due to the shear gargantuan amount of data produced, on the order of 10 GB to 200 GB per dataset. We have extended phase and grain orientation mapping by using a high-speed, high signal to noise CMOS-based electron detector. We could show that it does not only greatly improve the angular resolution, but also enables to locate nanotwins in a nanograined material [30] and opens the possibility to measure the local orientation of complex nano-phases embedded in a disordered matrix [43]. The analysis through commercial software packages of such large-scale datasets is often limited and we have therefore developed a Python-based open source, GPU-accelerated code with the aim to facilitate real time data analysis in the future. This will set the stage to combine *in situ* probing with 4D-STEM techniques to explore microstructure evolution dynamically with full crystallographic information.

Novel algorithms not only allow flexible and fast data analysis, but machine learning based approaches even provide the opportunity towards an autonomous data evaluation. Through collaborations within the BiGmax network with C. Freysoldt (CM department) and L. Ghiringhelli (FHI Berlin) we are developing supervised and unsupervised machine learning algorithms to segment and classify atomic resolution microscopy images. The unsupervised approach is based on local symmetry descriptors and is capable to automatically detect regions in images with deviating crystal structure or symmetry without prior knowledge of the underlying lattice structure [82]. This approach will be extended towards dynamic *in situ* observations and will be coupled to phase field models for being able to quantify and determine local properties of materials, here interface energies, while exposing the material to temperature in the electron microscope. The supervised deep learning approach is capable to classify image regions in atomic resolution STEM images and extracts local lattice constants and rotations. It is based on a convolutional neural network with simulated STEM images as ground truth training data. By coupling the classification to a Bayesian neural network, it is also possible to learn the location of defect and lattice disruptions, for example grain boundaries, through an uncertainty prediction. The supervised learning approach, which is so far based on Fourier space, will in a future collaboration with L Ghiringhelli be extended to a real-space classification, which is capable to also consider the intensity distribution of projected atomic columns in STEM images and hence local composition. The algorithm development is aimed to establish a self-learning and self-driving experimentation in the future.

Atomistic Modelling of Material Interfaces (T. Brink, since 01/2020)

Group mission: The group Atomistic Modelling of Material Interfaces was established in Jan. 2020 supported by the European Research Council (ERC GB-CORRELATE) to supplement the experimental work on grain boundaries in the department with atomistic computer simulations. Currently, we focus on investigating the thermodynamics of grain boundary phases using MD and density-functional theory (DFT) simulations. Several such grain boundary phases could be found using the HAADF-STEM imaging capabilities of the department, but the full three-dimensional structure as well as the thermodynamic excess properties of the grain boundaries remain inaccessible. Here, computer simulations can provide models of not only the phase stability, but also of e.g. mechanical behaviour of the grain boundary, which can affect macroscopic material properties such as grain growth or Hall-Petch hardening. Using this connection, the goal is to ultimately develop structure–property relations for grain boundaries.

Grain boundary phases

Most experimental evidence for GB phase transitions in metallic systems is indirectly inferred from changes in macroscopically measurable properties. While the fact that these changes can be measured underlines the importance of GB phase transitions, more direct evidence is required. Here, we worked on a $\Sigma37c\ \langle111\rangle\ \{1\ 10\ 11\}$ tilt GB in copper in collaboration with the *Advanced Transmission Electron Microscopy* group as an example which exhibits interesting phase behaviour. In both experiments on thin films and in computer simulations, two GB phases were found, which possess similar atomic motifs as for the $\Sigma19b[11\bar{1}]$ tilt GB (compare Figs. 2 and 4). Free energy calculations using the quasi-harmonic approximation show that these phases exhibit a congruent transition (i.e., no change of GB plane) at 450 K under ambient pressure. One novelty is that the transition of the $\Sigma37c\ \langle111\rangle\ \{1\ 10\ 11\}$ requires neither diffusion nor externally applied stress [27].

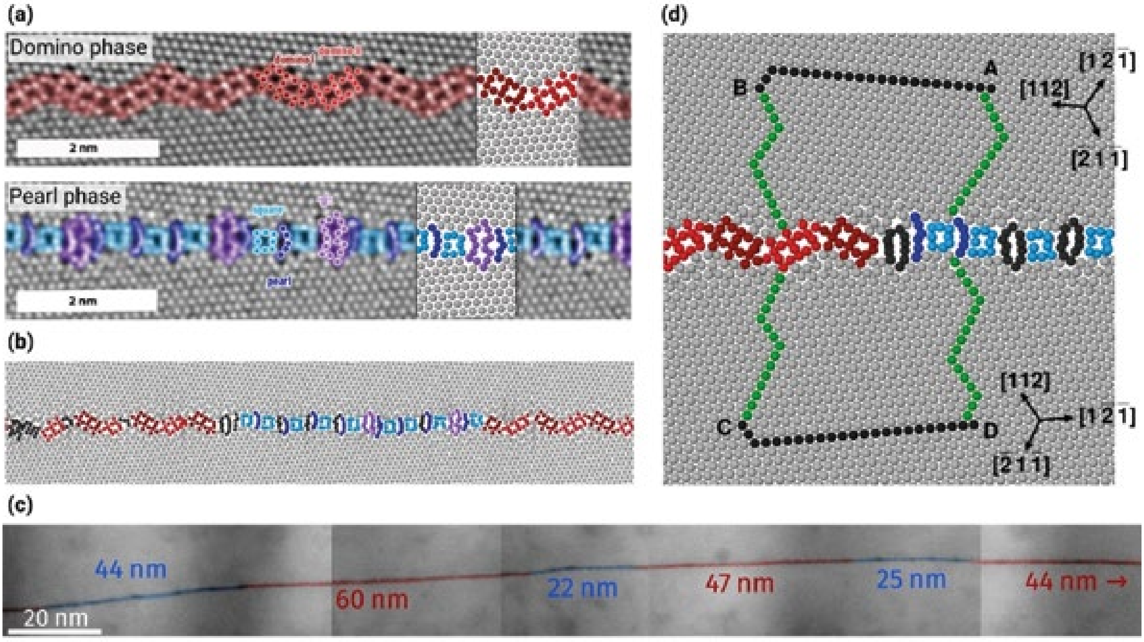

Fig. 4: *(a) Two grain boundary phases in a copper Σ37c ⟨111⟩ {1 10 11} tilt grain boundary found both experimentally and by computer simulation (insets). (b) Above 450 K a phase transition from Domino to Pearl phase occurs; here a simulation of the homogenous nucleation of the pearl phase is shown. (c) In experiment, the two phases form a pattern. (d) We analyzed the Burgers vector of the phase junction. From [27].*

Experimentally, though, a pattern of alternating phases is observed at room temperature (Fig. 4). Gibbs' phase rule excludes that such a microstructure can be stable and would lead to the assumption that the metastable phase remains in the system for kinetic reasons. Indeed, an analysis of the junction separating both grain boundary phases shows that this defect has a Burgers vector with a large screw component. Such line defects are expected to move comparatively slowly. Further analysis revealed that additional disconnections (dislocation-like defects in the GB), which exist to compensate asymmetry and/or a slight twist of the GB, can lead to repulsive interactions between defects and can potentially stabilize the phase pattern energetically. This shows that the complex interplay between defects and thermodynamics can lead to surprising effects in grain boundaries which need to be considered to fully understand these interfaces [27].

Presently, work is ongoing to broaden these analyses to other ⟨111⟩ tilt grain boundaries and fcc metals, such as aluminium. The goal is to differentiate general trends regarding the occurring phases and their stability from material-specific phenomena. In the near future, this work will also be extended from elemental metals to the addition of alloying elements. This is of particular importance for applications because temperature and stress state are almost always dictated by the use case, leaving only composition as a practical variable.

Structure–property relations at intergranular interfaces

The main practical importance of studying GB phases is the same as for bulk phases: The tailoring of material properties and the establishment of structure–property relations. We follow several different directions to elucidate these relationships.

It is well known that defects increase electrical resistivity, but the GB contribution is only known as an average value over larger sample volumes. First experiments on single GB resistivity measurements were performed in the *Thin Films & Nanostructured Materials* group (see p. 173) [1, 16]. While the resistivity could be measured as a function of crystalline misorientation and GB plane, the GB excess properties remain inaccessible to these experiments. We performed simulations on some of the high-angle boundaries studied experimentally and determined the stable phases at a high temperature approximately matching the annealing temperature of the experimental thin film. Using the derived GB excess properties, we could identify a correlation between excess volume or GB energy and resistivity [16]. We expect deeper, mechanistic insights from electronic structure calculations in collaboration with the CM department, which are currently ongoing.

Thermally activated grain growth is relevant for the evolution of a material's microstructure, while shear-coupled

GB motion can be a relevant mechanism of plasticity in fine-grained materials. Both are related to the GB mobility, which can be expressed as a tensor. In this project, we are interested in the influence of GB phase transitions on the mobility tensor. In many cases, grain boundaries migrate via the movement of disconnections, which can couple to an applied mechanical stress. Different GB phases can have different disconnection types, but even if these defects exhibit the same Burgers vector they can differ in nucleation energy and the energy barrier for their movement. Here, we study and characterize the defects responsible for the mobility and already found that the activation barriers of defects with the same Burgers vector can differ between different GB phases.

In the future, investigations on the influence of GB phase transitions, including for example faceting transitions, on dislocation nucleation and transmission are planned. Grain boundaries can act as obstacles to dislocations, thereby influencing macroscopic plasticity, or can act as sinks or sources for dislocations in fine-grained materials. We expect that this behaviour can be modified by GB phase selection.

Nano- and Micromechanics of Materials (C. Kirchlechner until 01/2020, J.P. Best since 04/2020)

Group mission

The overarching aim of the group is to quantitatively understand, predict and alter fundamental mechanisms governing plasticity, fatigue and fracture of materials. For this purpose, we isolate individual mechanisms – such as slip transfer of dislocations across a grain boundary – by performing small-scale mechanical experiments on samples under strict levels of geometrical and environmental control. But our work far surpasses the local measurement of strength and toughness: 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, local chemistry or phases, length and density of cracks and crack networks, etc.) which requires an advanced characterization toolbox with *in situ* capabilities.

An active and important mission of the group is method development. Over the last years 3D Laue microdiffraction techniques have been developed at the ESRF in Grenoble to determine decisive *in situ* material parameters (e.g. local strains, dislocation densities, grain boundary character, etc.) non-destructively with high spatial resolution (<1 μm). The 3D Laue micro diffraction activities at the SN department were led by C. Kirchlechner and will be continued at KIT. Additionally, *in situ* methodologies have been developed at the SN department for high-temperature measurement within an environmental chamber utilizing novel laser heating approaches, demonstrated for tensile testing of Cu thin films [3], along with further high-throughput tensile characterization of thin films [4]. The same environmental chamber used for this device is currently extended to microscale mechanical measurements under reactive environments (see p. 66), opening up exciting new challenges and possibilities in studying the interface between mechanics and chemistry during deformation and crack growth, for example. For these studies, new geometries are under active development to allow for stable crack growth, and will be exploited in the near future.

A developing theme within the group is the linking of local chemistry, imbued either through processing or environmental reaction in operando. In this space, environmental testing methodologies are being developed, including at temperatures ranging from −150 °C to 800 °C. For local chemistry variation, the deposition of thin films, which can be used to diffuse species to or along grain boundaries or dislocations is of active investigation.

Single and bi-crystal plasticity in metals

When single crystal sample sizes are taken down to the microscale, standard understandings of deformation no longer apply due to the probabilistic nature of dislocation plasticity. Therefore, motivated by sample size effects the group uses nanoindentation and micromechanical-based approaches to study the strength and deformation mechanisms of advanced material systems. This has been demonstrated for single crystalline Co-based Laves phases which have been studied as a function of crystal structure and composition [40, 41], but also for testing the critical resolved shear stress (CRSS) of basal and pyramidal I slip systems in pure Mg using a micro-shear testing geometry [6].

Within the framework of a recently-concluded SFB/Transregio TR188 project on dual-phase steels, significant progress has been made in understanding the CRSS of variant-containing martensite [89], and single crystal ferrite as a function of strain rate [90]. From these investigations, the activation volume for slip in ferrite was determined, along with insights into non-Schmid plasticity activation with increased strain rates. The CRSS for single phase regions of bainite have also been studied through an industrially funded collaboration. The gained information provides novel basic information and serves as inputs into crystal plasticity simulations with F. Roters in the MA department. In that work, phase identification of the complex bainitic steel microstructure was made through nanoindentation linked to machine learning clustering algorithms. As recent results have shown that indentation close to grain boundaries has a significant effect on the accuracy of such clustering approaches, we are currently trying to isolate boundary conditions where such machine learning approaches may be utilized.

Indeed, understanding deformation in the vicinity of grain and phase boundaries constitutes a significant body of work within the group, as important open questions currently exist on how GB structure and chemistry influences transmission mechanisms, and the local strength. Within this realm, the group has studied in detail Cu micropillars which contain a single GB. Coherent Σ3 (111) twin boundaries in Cu have been shown through extensive study to allow cross-slip-like transmission, leading to low transmission stresses and similar deformation behaviour to that of single crystals. However, when thin-films of Ag containing closely spaced nanotwin arrays were produced, micropillar compression experiments showed high strengthening due to dislocation bowing in each single crystal zone during the continuous slip [10, 64] (Fig. 5). Cross-slip in Cu is currently being extended to higher-energy incoherent Σ3 (211) twin boundaries, where the transmission stresses and mechanisms are being investigated for magnetron sputtered thin-film systems where such non-equilibrium boundaries can be produced in a controlled manner. Twin boundaries can also act as dislocation sources, while recently published work on Cu showed that spherical nanoindentation on such boundaries allows a source activation stress smaller than that needed for bulk single crystals, irrespective of indenter size, dislocation density and stacking fault energy [91, 92]. The role of chemistry on dislocation activation at, or transmission through, grain boundaries is a current focus using micropillar compression and high-throughput nano-scratching supported by advanced microscopy.

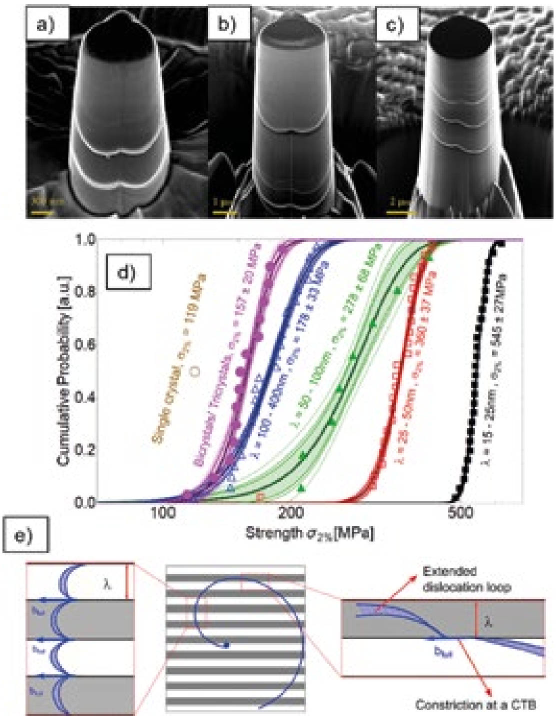

Fig. 5: *Dislocation plasticity at twin boundaries. Post mortem SEM micrographs of bi-crystal micropillars with nominal diameters of 1 µm (a), 3 µm (b), and 5 µm (c) compressed to a strain of 5-10 %. For Ag thin-films containing nanotwins, cumulative probability distributions of $\sigma_{2\%}$ strength data divided into twin spacing λ bins are shown (d). Proposed plasticity mechanism in closely-spaced nanotwin containing Ag thin films (e); dislocation loops close to a conjugated slip system are projected onto a pillar slip plane showing several constrictions at CTBs [10].*

Microscale fracture mechanics

Failure through fracture of engineering components and structures has an enormous cost to society. Such processes are initiated at small scales at atomically-sharp crack tips, where plasticity and decohesion processes are involved at the stress concentrations which develop under loading the notched component. Therefore, there is a significant link between local plasticity and fracture. Linear elastic fracture mechanics (LEFM), or fracture prior to plastic deformation, is an established method at small-scales in the group [93] and is used to study advanced materials and material microstructures such as grain boundaries [17].

For brittle materials, plasticity is limited due to the difficulty of activating dislocations in stiffly bound covalent systems, and therefore fracture occurs during the elastic region governed by LEFM. This has been demonstrated for a number of thin-film ceramic systems such as multi-metal carbides [67, 94], and AlN-based coatings [95]. Using these principles, the group has assessed the reliability of annealed metallic interconnect thin-films in an industrially funded basic research project, where the fracture toughness from single cantilever bending experiments is linked to the structure and chemistry of the initially amorphous Ni-P alloy as a function of temperature. Current work looks at linking the brittle-to-ductile transition as a function of temperature and strain rate for bulk-scale intermetallic systems, as for our project within the DFG-funded SFB 1394 focused on Laves phases in the Mg-Al-Ca system (see p. 76).

When fracture necessitates significant plastic deformation around the crack tip, then elastic plastic fracture mechanics (EPFM) is utilized. EPFM is at the frontier of understanding for micro-geometries, but has huge promise for understanding fundamental processes during fracture for tough materials systems. Within TR188, together with our advanced understanding of the CRSS in single crystal ferrite regions, novel cantilever-based micro-geometries have been developed to allow for EPFM analysis of microscale martensitic islands [96]. Similar approaches are currently used to perform local fracture of single grain boundaries in tungsten. Recent projects have also looked at white etching layers in steel rails [97, 98], together with an overarching aim of further developing EPFM based on optimization of the notch and testing geometry for improved reliability of EPFM tests [5].

Advanced testing of functional oxides

Oxides find broad applications as catalysts or in electronic components, however are generally brittle as dislocations are difficult to activate in the rigid covalent lattice. Here, the link between plasticity and fracture is critical for wide-scale application of functional oxide materials. Together with our Max Planck partner group *Damage Tolerant Functional Oxide Nanostructures* (head: N. Jaya Balila) at the IIT Mumbai (see p. 32) we have analyzed room temperature deformation in $BaTiO_3$

where near-theoretical strength is achieved for sub-micron pillars, and significant plasticity reported as the length scale increases past 1 µm [99]. Ongoing research looks at the temperature-dependent microscale fracture toughness of $BaTiO_3$ around the Curie temperature where a tetragonal to cubic phase change is expected. Additionally, we study sub-micron single crystal pillars of the transparent semiconductor Ga_2O_3 under variable strain rate conditions, to elucidate subtle transitions in active dislocation mechanisms during compression, which may be later linked to improved processability of the single crystal with applications in optoelectronic devices [100].

We also focus on how defect structures in oxides affect the functional properties. Together with collaboration partners in Darmstadt, we have determined that the dislocation structure formed under low-load indents into TiO_2 [101] can have a strong effect on the electrical resistivity. High temperature measurements are also ongoing on single crystals of various iron oxide phases. $Fe_{1-x}O$ (Wüstite) is a critical phase for a number of applications. In the CO_2-free H_2-based iron ore reduction, for example, $Fe_{1-x}O$ is the rate-determining intermediate phase in the production of iron for the steel industry. While for H_2 production by water-splitting, $Fe_{1-x}O$ is a potential photochemical material. For both of these processes, the transport mechanisms of Fe ions within $Fe_{1-x}O$ and therefore the atomic structure of $Fe_{1-x}O$ are key to understand. In studying how the variations in oxide stoichiometry affect the defect structure and mechanical properties of the Wüstite phase, mechanical investigations on bulk-scale single crystals are also here complimented by reactive magnetron deposited iron oxide thin films for precise control over both the structure and chemistry of the resultant phase.

Nanomechanical Instrumentation and Extreme Nanomechanics (XNano) (R. Ramachandramoorthy, since 08/2020)

Group mission

Pushing the envelopes of micro/nanomechanical testing to relevant, but so far unexplored strain rate and temperature combinations is one central mission of this new group. In addition, additive micromanufacturing across meso-, micro- and nanoscales to obtain novel structural and functional lattice structures constitutes our second goal. For an overview of the group's research focus and the motivating factors, refer also to the section on new research groups (p. 46). Given the unique challenges presented by small scale sample fabrication and their characterization under extreme loading conditions, a significant effort in our group is focused on instrumentation, methods and protocol development. It is our vision to use such novel infrastructure and testing methods to uncover the fundamental microstructure-property relationships of micro- and nanoscale materials under application relevant strain rates and temperatures, which currently remain largely unexplored.

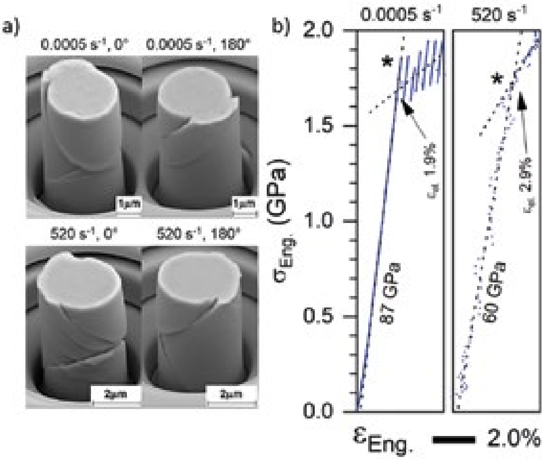

Fig. 6: *a) SEM images of bulk-metallic glass micropillars compressed at strain rates of 0.0005/s and 520/s and their corresponding stress-strain signatures are shown in b) [8].*

Dynamic micro- and nanomechanical testing

A fundamental understanding of the microscale deformation mechanisms during high-speed impacts is vital for developing protective technologies for demanding applications such as micrometeorite impact with spacecrafts, cold spray coating technology and microparticle impacts on aircraft turbines. Regardless, owing to the lack of testing platforms, the majority of micro- and nanomechanical testing focuses only on quasi-static testing [102]. To conduct micromechanical testing under extreme strain rates >10.000 s^{-1} with the simultaneous capture of high-speed load and displacement signatures (see Fig. 6 for bulk-metallic glass example [8]), we have performed extensive hardware modifications to an *in situ* micromechanical testing system [8, 103]. This includes the introduction of a high-speed voltage supply for activating a piezo-based actuator at high speeds (up to 100 mm/s), piezo-based load-sensing system and support electrical systems for high-rate signal generation (~25 MHz) and acquisition (~5 GHz). Additionally, protocols and methods specific for such extreme micromechanical testing are currently developed to address problems such as system resonances, inertia, wave propagation and low signal-to-noise ratio.

Nanomechanical testing is an invaluable tool for understanding the fundamental deformation processes in 1D and 2D materials such as nanowires and nanoparticles. But such nanoscale mechanical metrology even for quasi-static tests requires specialized testing platforms that are capable of applying displacements with nanometer resolution and resolving loads with nano-Newton sensitivity [104]. To address such stringent requirements, in conjunction with company partners and supported by EU funding, we are currently developing an *in situ* microelectromechanical system (MEMS)-based high-speed testing platform with electronics-based capacitive load sensing

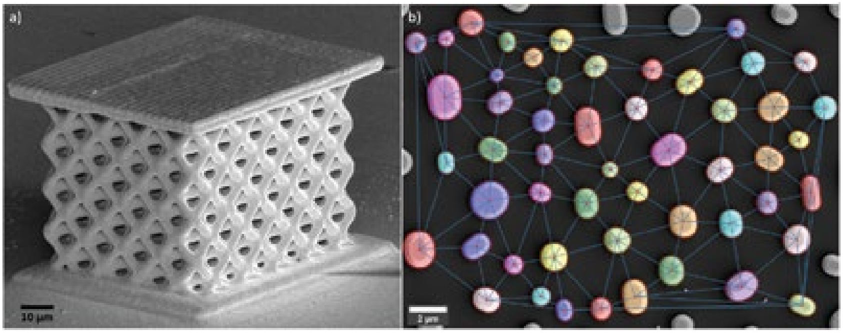

Fig. 7: *a) Full-metal copper micro-lattice fabricated using additive micro-manufacturing. b) Dewetted nickel microparticles post-processed for size, shape and density analysis.*

capability (~500 kHz bandwidth) and piezotube-based high speed actuation (up to 100 mm/s), to be used inside an SEM and TEM.

Additive micro-manufacturing

Full-metal micro/nano architectures have profound applications in metal MEMS based devices, MEMS packaging for energy absorption/impact resistance, photonics, plasmonics, catalysis and corrosion studies. Conventional additive manufacturing, though it guarantees geometric freedom and spatial control, is limited to a minimum feature size of 20 µm. Thus, there is a critical need to identify a method for 3D printing metals at the micro- and submicron scale (down to ~200 nm feature size) to create complex – and otherwise hard to reach – geometries (~1 µm to 1 mm overall dimensions) such as meso-/micro-/nano-lattices, microsprings etc. [105]. To address this requirement, we explore a localized electrodeposition-based additive micro-manufacturing technique (Fig 7a). In this method, an electrochemical ink with metal ions is pushed through a hollow microchanneled atom force microscopy (AFM) probe, which gets reduced onto a conductive substrate layer (working electrode). The voxel-by-voxel manner of metal deposition allows the fabrication of complex 3D microarchitectures with a voxel diameter of 200 nm to 15 µm, depending on the aperture size in the AFM probe. Using this method, any electrodepositable metal can be printed into arbitrary-shaped small-scale architectures and so far, we have successfully fabricated full-metal complex 3D copper micropillars and microlattices (see p. 64 for additional application of fluid-filled architecture). We will further investigate the suitability of such full-metal architectures towards energy absorption and mechanical band-gap engineering applications, using *in situ* and *ex situ* dynamic testing inside an SEM and under an optical microscope (see p. 66 for environmental chamber being developed for this purpose) respectively.

Dynamic thermomechanical characterization of dewetted microparticles

Another promising technique to obtain a large number of pristine micron scale metallic samples is using solid-state dewetting of thin films [63]. In collaboration with the *Thin Films & Nanostructured Materials* group in the SN department, we have developed specific protocols for dewetting nickel thin films to produce single-crystal nickel microparticles. To optimize the dewetting protocols we use python-based algorithms to identify the particle size, shape and density in an automated manner from SEM images illustrated in Fig. 7b. We plan to apply similar thin film dewetting methodologies to soon obtain iron and iron oxide microparticles. Currently, a high throughput mechanical testing study is underway to obtain the dynamic properties of such dewetted nickel particles at a variety of strain rates (10^{-4} s^{-1} to 10^{+4} s^{-1}) and temperatures (-150 °C to 800 °C) using the custom modified *in situ* micromechanical tester inside an SEM. We hope to uncover the deformation signatures of single crystal nickel under these extreme loading conditions using a combination of the thermal activation parameters extracted from the stress-strain signatures and post-test microstructural characterization using TEM and Kikuchi diffraction techniques.

Hydrogen Mechanics and Interfaces (M.J. Duarte Correa, since 09/2019)

Group mission

We correlate the microstructural properties of metals and alloys and their interaction with environmental factors, particularly hydrogen. A key element is the study of interfaces, since they are largely responsible for material strength. The final goal of our research is to minimize the deleterious effects of hydrogen and provide guidelines for hydrogen tolerant materials. The group was established in September 2019 supported by the European Research Council (ERC GB-CORRELATE).

The mechanical behaviour of a material can be significantly altered by the presence of hydrogen (Fig. 8), causing catastrophic and unpredictable failure, known as hydrogen embrittlement. This represents a significant challenge for the implementation of hydrogen as a sustainable energy source. The large infrastructure required for a hydrogen economy, as well as the use of structural materials in environments that promote hydrogen uptake, require the understanding of the complex embrittlement phenomena at the nano- and microscale level; failure often starts at this length scale with accumulated local hydrogen which can evolve into macroscopic damage. Our work is focused on the understanding of individual damage mechanisms by performing small-scale mechanical experiments. We target specific underlying and evolving microstructural features (Fig. 8) and their mechanical response upon hydrogen ingress. Mechanical characterization is performed at length-scales below a few **μm** by nanoindentation and related techniques, such as nanoscratching, pillar compression and fracture testing [7, 15]. However, as the analyzed volume becomes smaller, the risk of hydrogen desorption becomes more relevant. A particular challenge is then to provide a continuous hydrogen supply during mechanical loading to minimize desorption and the associated formation of strong hydrogen concentration gradients at the testing regions.

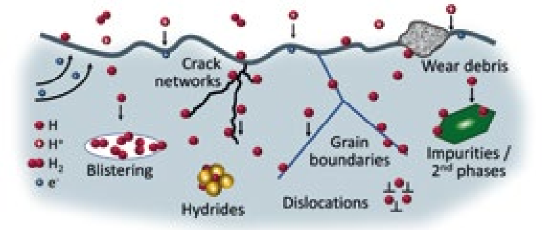

Fig. 8: *Schematic of hydrogen interactions with different microstructural features in metals.*

Instrumentation

We develop unique instrumentation and advance current tools to promote different atmospheres during mechanical testing and to introduce hydrogen into the material. We built two custom electrochemical cells for *in situ* hydrogen charging during nanoindentation, designated as "front-side" and "back-side" charging [7] mounted in a standalone nanoindenter. The front-side charging with the sample and indenter tip immersed into the electrolyte utilized similar concepts to existing setups. Due to direct contact of the tested surface with the electrolyte, hydrogen charging in the region of interest is fast, but has the disadvantage of often generating surface degradation. In the back-side charging approach, newly developed in the group, the analyzed surface is never in contact with the solution and the observed effects are only due to hydrogen. Hydrogen diffusion from the charged back-side towards the testing surface is quantified by permeation tests. Moreover, this unique method allows differentiating between the effects of trapped and mobile hydrogen, and performing well controlled measurements where different hydrogen levels can be monitored over time to consider hydrogen absorption, diffusion and release through the metal. We are currently implementing the back-side setup into a new instrumented nanoindentation platform inside a custom-made environmental chamber providing different atmospheres such as oxygen, inert or forming gases and dry air. In further developments, we aim to introduce this setup into a SEM.

Plastic deformation during hydrogen charging

A key question of this work is how hydrogen interacts with dislocations. The hydrogen influence on the plastic and elastic behaviour is studied at specific charging conditions using the back-side setup. Through nanoindentation we analyse the elastic modulus, hardness, incipient plasticity and dislocation nucleation, which when combined with pillar compression we further investigate the effect of hydrogen on the yield strength, i.e. insights into dislocation propagation and interactions. Current work is performed in model alloys to reduce the complexity of e.g. steels. We focus currently on Fe-Cr, Fe-Ni and Ni based alloys representative of body centred and face centred cubic structures. As an example, enhanced dislocation nucleation and hardness increase was observed while increasing the hydrogen uptake in Fe-Cr (Fig. 9 top). We established a linear relationship between the hardness increase and the hydrogen supply, and identified a hydrogen saturation level in Fe-Cr alloys. This hardening effect was modelled and attributed to an enhanced dislocation multiplication, pinning on the dislocation motion and an increase in lattice friction related to hydrogen.

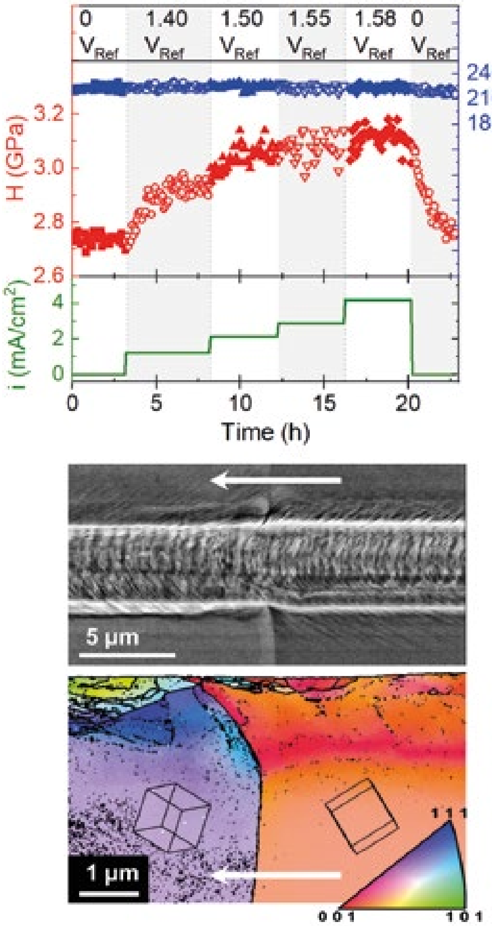

Fig. 9: *(Top) Hardness variation with current density (i.e. introduced hydrogen) and, (bottom) nano-scratch across a grain boundary and corresponding transversal inverse pole figure that shows recrystallization and the deformation extent. (All during cathodic polarization for hydrogen charging of a Fe-20 wt.% Cr alloy).*

Decohesion and failure at interfaces due to hydrogen

One of the most critical damage nucleation sites are interfaces. Most engineering and structural alloys contain a large density of grain and phase boundaries, affecting dislocation motion, generation and annihilation, and largely contributing to their mechanical strength. These interfaces can be seriously embrittled by hydrogen resulting in a significant degradation of the global mechanical properties. This prompts to question how the interface character, elemental segregation and hydrogen trapping behaviour influence failure and interface decohesion. We perform targeted measurements in model alloys and steels to probe this question. The important role of dislocation-interface interactions is initially examined by high-throughput scratch tests. The initiation of an intergranular crack is favoured if dislocation slip transmission is suppressed by the local stress incompatibility at the interface and enhanced by the accumulation of hydrogen. This might result in dislocation pile-ups at the interface and can be evidenced by a curved grain boundary after scratch testing (Fig. 9 bottom). Interface failure by crack initiation and propagation are further examined in specific decohesion experiments.

Hydrogen barrier coatings

In collaboration with the group Nanoanalytics and Interfaces (C. Scheu, MPIE), the Leibniz Institute in Greifswald, and the Helmholtz Center HEREON in Geesthacht, we study how to prevent or limit the hydrogen entry into structural alloys by the use of barrier coatings. Our initial studies reveal that bilayer Al-alumina coatings sustain exposure to 300 bar H_2 at 400 °C for 6 days; equivalent to Ar exposure under the same testing conditions. However, dewetting of the Al film occurs which indicates that pure alumina coatings are better suited. This is currently under investigation.

The mechanical findings in each project are complemented with other characterization techniques through multidisciplinary collaborations with all the departments at the MPIE and the group network. This includes especially thermal desorption spectroscopy and Kelvin probe measurements (M. Rohwerder, GO department) as well as APT studies (B. Gault, MA department).

Nanotribology (S. Brinckmann, until 12/2019)

Group mission

The investigation of microstructure evolution during wear of surfaces using well-defined and inert micrometre asperities that mimic the single asperities of macroscale components is the central mission of the *Nanotribology group*. These fundamental investigations of dry materials tribology address the irreversible microstructure mechanisms such as dislocation plasticity and twinning, grain refinement, as well as phase formation and dissolution [106-110].

Microstructure evolution during the initial stages of tribology

Understanding the transition from indentation to ploughing and the corresponding evolution of plasticity in austenite stainless steel for different grain orientations is one of our central research topics (Fig. 10).
We find that slip-step and pile-up evolution during the indentation segment influence plasticity during the subsequent ploughing segment [106]. Four stages can be seen during ploughing: first deformation by indentation, a transition region, steady-state ploughing at a rather constant depth, and finally the unloading segment. The lateral motion of the ploughing results in a break of deformation symmetry as documented by the pile-up and glide steps at the surface (Fig. 10). The deformation pattern is very distinct to that after indentation.

These findings highlighted the need to thoroughly understand the first contact of an asperity with the metal surface, and we hence extended the knowledge of nanoindentation and the microstructure evolution during this deformation stage. Towards this goal, we deformed grains with specific low indexed crystal orientation to

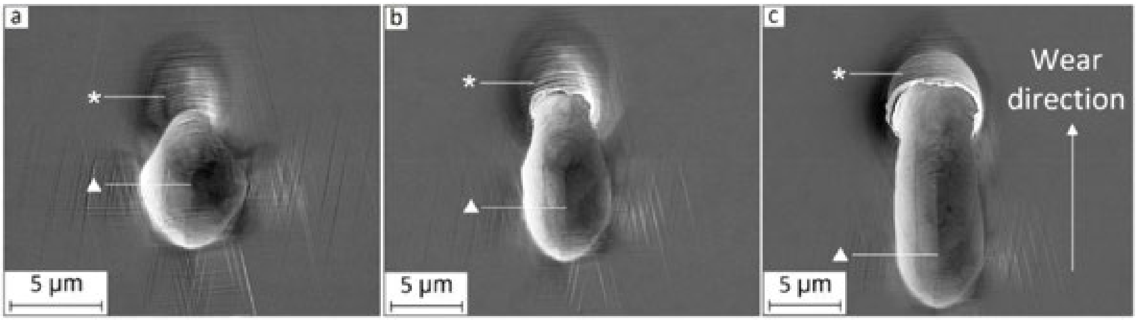

Fig. 10: *Secondary electron images of wear tracks with a 40 mN normal force in a [001] γ-Fe grain; a) 2 µm, b) 6 µm, c) 10 µm wear length. The white arrow in (c) denotes the wear direction for all tracks, the white asterisks and triangles mark the pile-up and the position of the initial contact, respectively.*

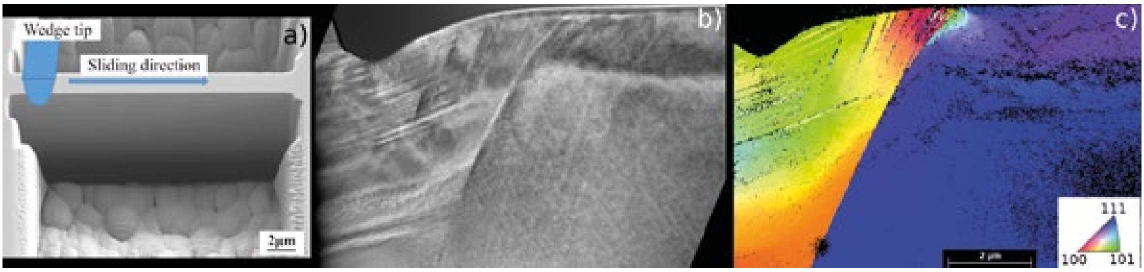

Fig. 11: *Tribology experiments on microwall: a) SEM image of microwall consisting of two twinned crystal orientations before deformation; b) dark-field TEM image of deformation and twin boundary and dislocation structure; c) Transmission Kikuchi diffraction (TKD) orientation map of the twin boundary and deformation in the left-hand grain.*

better understand the dislocation mediated plasticity through slip step analysis on different slip-plane inclinations [107]. We found that slip steps emerge first on slip planes starting from below the indenter towards the surface (positively inclined slip planes), while at a later deformation stage slip steps emerge from outside the indented zone towards the indent (negatively inclined slip planes) due to the change in surface topography. We calculated the resolved shear stress in the presence and absence of pile-ups and confirmed that the surface topography is the origin of the activation of the different set of glide planes [107]. We concluded that accounting for the surface topography evolution in experiments and simulations is essential in predicting the plastic slip activation during nanoindentation.

As the surface topography plays such an important role, a better understanding of the pile-up formation is warranted. We revealed by experiments that the shape of the pile-up changes at a critical inclination angle 55°-58° from radial plastic flow to circumferential plastic flow for the different grain orientations [108]. As the plastic flow of other activated slip-planes change similarly, the interaction of these slip-planes determines the final pile-up shape. These experimental findings, which are based on SEM surface topography and SEM-ECCI (electron channelling contrast imaging) analyses were augmented by finite element method (FEM) simulations to better understand the stress state during indentation and the influence of the topography. The FEM simulations reveal that the resolved shear stress inverts around this critical angle for the different grain orientations studied.

As the deformation of the microasperity transitions from indentation to wear, i.e. transitions from stationary to sliding contact, the conservation of contact area, elastic recovery, and the front pile-up development dominate the deformation mechanisms [109]. By investigating this transition in copper, cementite and austenitic steel, we concluded that the elastic recovery leads to an additional contact area at the backside of the asperity. The influence of the crystallographic orientation was found to be negligible during the initial increase in wear depth but significant during the later stages. Moreover, a partial elastic wear depth recovery was observed in ductile materials.

Evolution of twinning during wear

Twinning and the resultant microstructure evolution can lead to the formation of a hard surface layer that protects the material during continued tribological loading. We investigated the influence of wear direction on the deformation mechanisms in single austenite steel grains (Thermax) with {001} and {111} normal orientation and observe multiple intersecting twin structures below the wear track. The extent of deformation and the twin density was found to be dependent on the wear direction, normal load and asperity geometry. The competition of twinning and dislocation plasticity is the origin for the differences between grain orientations: some grains show predominantly twinning while others preferentially exhibit dislocation plasticity.

Simplifying the stress state during plasticity to improve the understanding of wear mechanisms

Single nano-/ microasperity sliding wear tests allow to separate the microcontacts and to study the origins of plastic evolution during the initial stages of tribology. We pre-remove material before scratching to obtain microwalls of finite width (approximating a 2-dimensional structure) (Fig. 11). This simplifies the stress state and allows to directly inspect the contact zone from the top and the side. After sliding on the microwalls, a misorientation jump forms underneath the wear track by formation of a grain boundary. The crystallographic misorientation reached 30° in some configurations, resulting in the formation of large angle grain boundaries. We unravelled the grain formation mechanism via slip-step and dislocation analysis by addressing dislocation arrangements at the grain boundary.

Thin Films and Nanostructured Materials (M. Ghidelli from 01/2019 until 01/2020, J.P. Best since 04/2020)

Group mission

We focus on the development and synthesis of novel nanostructured thin films, while exploring their physical and mechanical properties [1, 16, 52, 95]. Motivating the group's work is the requirement of novel high-performance thin films with superior structural and functional properties for advanced applications such as micro-/nanoelectronics, energy production, sensors and wear protection [25, 52, 57, 59, 60, 63, 95]. In particular, intrinsic but mutually exclusive structural properties such as high strength and ductility must be combined, but also the resistance to harsh conditions such as corrosive environments, wear, and high temperature be improved. Our research also includes thermal stability against decomposition, grain growth and dewetting.

Key for property control is the film architecture and microstructure. To afford control over the material properties the microscale porosity, atomic composition, average grain size, phase distribution, and layer/film thickness must be optimized. In achieving such a high level of control, the group leverages a unique physical vapor deposition cluster to perform magnetron sputtering and electron-beam deposition of both metals and ceramics. We further ongoing links on alloy development and novel alloy combinations forged together with the MA department, where novel high entropy alloys and amorphous metal thin films are deposited for high-strength high-toughness combination materials.

tensile tests on flexible substrates, and X-Ray diffraction as a function of temperature. From these experiments we have found that the content of Cu (at.%) influences the atomic arrangement, and the resulting mechanical properties and thermal stability, which we currently aim to link to the characteristic atomic-scale order through high-energy synchrotron measurements.

Moreover, we managed to fabricate complex film architectures from the $Zr_{100-x}Cu_x$ system, such as multilayers and amorphous-nanocrystalline composites, to investigate the role of interfaces and secondary phases as obstacles to shear band propagation for further enhancement of the mechanical properties. The breakthrough of amorphous multilayer (ML) film synthesis with bi-layer period down from 200 to 5 nm will allow us to correlate interfacial effects on the mechanical properties in all-amorphous TFMGs (Fig. 12a). In collaboration with the MA department, we used a new strategy to develop thermally stable, ultrastrong and deformable crystal-glass nanocomposites through a thermodynamically guided alloy design approach. We realized this in form of a model CrCoNi (crystalline)/TiZrNbHf (amorphous) nanolaminate composite alloy with bilayer period of 5 nm. This unique nanoarchitecture shows an ultrahigh compressive yield strength of 3.6 GPa and large homogeneous deformation to ~15% strain, surpassing those of conventional metallic glasses and nanolaminates while exhibiting a high crystallization temperature >973 K.

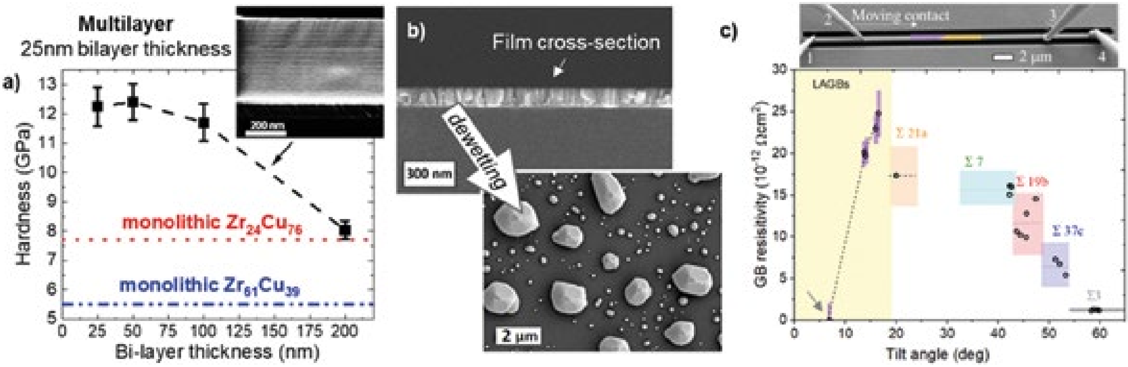

Fig. 12: *Nanoindentation hardness for single and ML ZrCu TFMGs (a). The hardness of MLs with bi-layer thickness of 25 nm (inset, SEM cross-section image) is higher than the rule of mixture for the two components, reaching ~12 GPa. SEM cross-section image of Co-Cu film (~15 at.% Co) showing a densely packed columnar structure (b), together with image after SSD highlighting islands formed after annealing. Microscale in situ electrical resistivity measurements (c) show that the resistivity of specific GBs in Cu varies with tilt angle [16].*

Thin film metallic glasses and nanolayer engineering

Amorphous thin film metallic glass (TFMG) alloys are exciting candidates for next-generation applications, such as flexible electronics, due to their advantageous mechanical properties such as combined high yield strength (up to 3 GPa) and ductility (up to 10 %) [111, 112]. However, the relationships between film chemistry, microstructure and mechanical properties have barely been investigated in this materials class. To address this, we have deposited $Zr_{100-x}Cu_x$ TFMGs with controlled composition by magnetron sputtering, and linked the atomic structure (chemistry) with mechanical properties and thermal stability using nanoindentation, surface Brillouin spectroscopy,

Electrical characteristics of thin film systems

Together with the mechanical performance, the investigation of electrical properties constitutes a major focus, linking to electronic applications such as metallic interconnects or flexible electronics. In the group, we focus this study onto defects in metallic alloys and oxides with special attention on GB engineering. Thin films are deposited by sputtering and then annealed, enabling the production of columnar GB segments which can be investigated at micron and sub-micron scales by *in situ* SEM resistivity measurements developed in-house [1]. Among our achievements is the attainment of abnormal grain growth for epitaxial pure metal (Cu, Ti, Ni and Al) thin films. Moreover, we have enabled the synthesis of desired GB types, whose local electrical properties have been investigated (Fig. 12c) and compared to MD simulations of GB structure performed by T. Brink in the SN department [16]. On-going research involves elucidating the effects of chemical segregation on local resistivity, and in working towards this we have developed a deposition methodology to obtain abnormal growth in Fe-diluted Cu alloys overcoming the pinning of GBs by segregation.

Intermetallic Materials (M. Palm, F. Stein)

Group mission

The investigation of fundamental aspects of the thermodynamic stability of intermetallic phases in view of their possible use for structural applications is the mission of the group Intermetallic Materials.

TiAl-based alloys

Aligned with our group mission, the large-scale international collaborative project ADVANCE (https://thermocalc.com/about-us/advance/) aims at improving a thermodynamic database for the computer-driven development of TiAl-based alloys (see p. 89). In all, the constitution of ten Ti–Al–X(–Y) (X = Nb, Mo, W, O, B, Zr, C, Si; X/Y = Nb/W, Nb/Mo) systems will be investigated. The investigations focus on establishing the phase equilibria and phase transformations in the Ti-Al-rich parts of the systems between 700 – 1400 °C.

Ti–Al–Nb/Mo/W: Currently applied TiAl-based alloys are multicomponent materials with Nb as a major alloying component. Consequently, a detailed knowledge of the phase relations in the ternary Ti–Al–Nb system is of utmost importance. Within the ADVANCE project, the complex ternary phase diagram of this system is constructed by combining results from equilibrated alloys and diffusion couples in the temperature range 700 – 1300 °C [73]. Special care has to be taken regarding the oxygen impurity contents, which were proven to affect the phase equilibria [38]. Another issue is the occurrence of two ternary intermetallic phases (so-called ω0 and O-phase) in the Ti–Al–Nb system, which decompose in the solid state near the regime of desired application temperatures [113, 114]. Moreover, the effect of partial replacement of Nb by Mo or W and the phase diagrams of the ternary systems Ti–Al–Mo and Ti–Al–W are currently under investigation. A comprehensive assessment of the Ti–Al–Mo ternary system has already been performed [78], and existing phase diagram descriptions of the Al–Mo and Ti–Al–W systems were updated [76, 115].

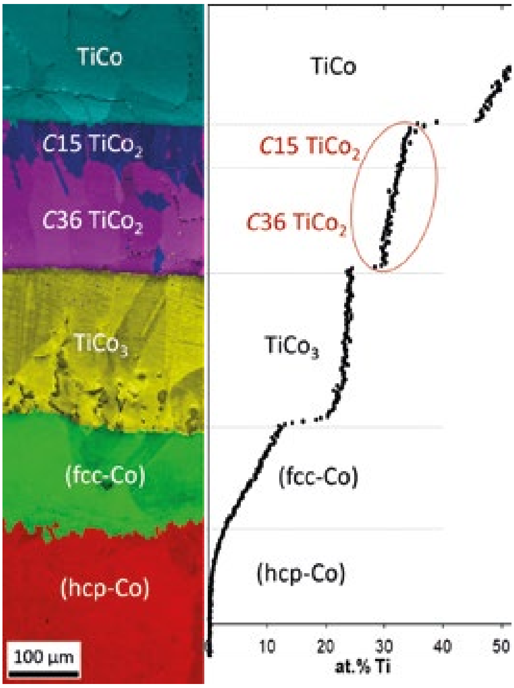

Fig. 13: *EBSD phase map of a Co-TiCo diffusion couple (144 h at 1100 °C) and respective concentration profile revealing the co-existence of C15- and C36-TiCo2 Laves phase without a step in the concentration curve [117].*

Ti–Al–Si: In this system five partial isothermal sections between 800 – 1200 °C have been established. On equilibrated alloys the phases have been identified by X-ray diffraction (XRD), compositions of the coexisting phases were established by electron probe microanalysis (EPMA) and temperatures of phase transformations were determined by differential thermal analysis [77]. Consistency of the isothermal sections was checked by setting up a vertical section for 9 at.% Si.

Ti–Al–Zr: Investigation of this system started with a critical assessment of the published literature [42]. The ongoing investigations already revealed that phase equilibria are actually quite different from previously published ones [74]. The underlying reason is that phases had been taken into account which are stabilized by impurities. This became apparent as in the present investigation high-purity materials are used and the impurity content is minimized by respective measures during heat treatments and controlled by wet-chemical analysis after annealing [74].

Ti–Al–O: Work on this system again started with a critical assessment of the existing literature [submitted]. As it is a key system not only for TiAl-based alloys, but also for Al_2TiO_5 ceramics, a large number of references are available for this system, which had not been assessed since more than 20 years.

Finally, a critical assessment of the Ti–Al binary system has been updated [116].

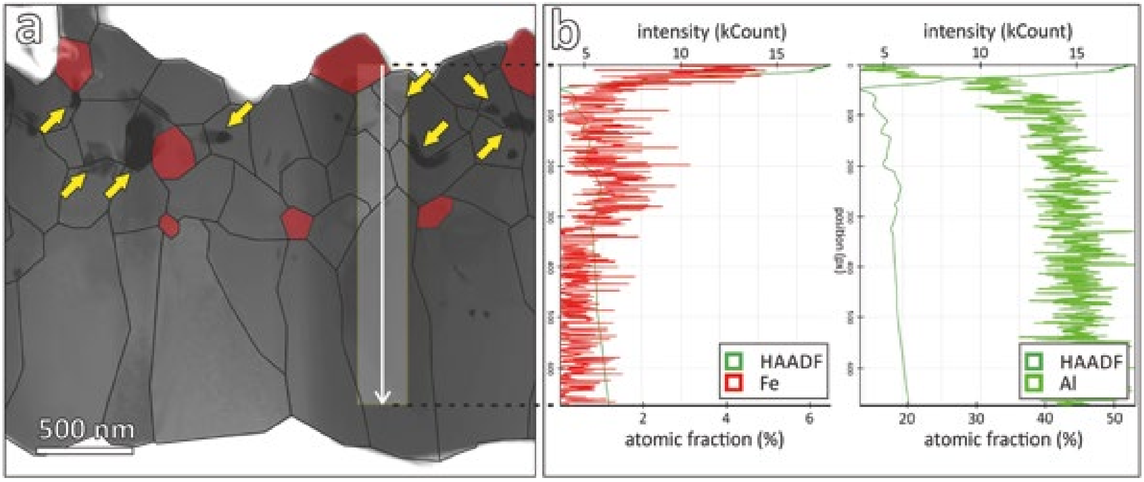

Fig. 14: *a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) micrograph with marked b) STEM energy-dispersive spectrometry (EDS) line scan of Fe-Kα and Al-Kα calculated as atomic fractions, showing the presence of Fe in the upper layer of the scale, while pillar-like alumina at the bottom is pure* Al_2O_3*. To better visualise the grain structure, grain boundaries are marked by lines, and spinel grains have been coloured red. The black patches in the underlying STEM micrograph are corrosion pits (marked by yellow arrows) [49].*

Laves phases

Another research focus of the *Intermetallics group* is on the thermodynamic stability and properties of Laves phases, which form one of the largest groups of intermetallic phases and can exist with three different crystal structure variants (cubic C15, hexagonal C14 and hexagonal C36). In several systems, two or even all three variants can co-exist as equilibrium phases in adjacent composition ranges. An example is the co-existence of C15-$TiCo_2$ and C36-$TiCo_2$ Laves phases in the Co–Ti system [33, 117] (Fig. 13). The phase fields of these two polytypes should be separated by a two-phase field as there is no crystallographic group-subgroup relation between the space groups of the cubic C15 and hexagonal C36 structure type. However, the concentration profile measured on a Co/TiCo diffusion couple (Fig. 13) does not indicate any step-change in composition. A possible explanation might be the presence of a coherent equilibrium between the two structurally closely related phases [117]. Other Laves phase related projects of the group concentrated on the composition and structure dependence of mechanical properties of the C14, C15, and C36 polytype of the $NbCo_2$ Laves phase which exists in an extended homogeneity range of about 10 at.% [40, 41, 118], on the occurrence of extended planar faults in off-stoichiometric $NbFe_2$ Laves phase (where preliminary results were already mentioned in the last Scientific Report) [37], and on the special deformation behaviour of the mono-clinic phase Nb_2Co_7 which possesses a Laves phase related crystal structure [34, 36, 45]. Finally, the group was invited to write a comprehensive overview on Laves phases, which was published in 2021 [48].

Iron aluminides

One of the long-standing research activities at the MPIE is the investigation of fundamental aspects for the development of sustainable iron aluminide alloys. In the framework of a large-scale industrial cooperation devoted to the development and processing of advanced iron aluminide alloys [44, 119, 120], specifically the metastable precipitation of the Heusler phase which is decisive for fine-tuning the microstructure, and has been investigated by atom probe tomography (see p. 186).

Their outstanding corrosion resistance is one of the features that makes iron aluminides so sustainable. However, their aqueous corrosion behaviour is only mediocre and whether it can be improved through pre-oxidation has been controversially discussed in literature due to conflicting experimental evidence. Therefore the aqueous corrosion behaviour of pre-oxidized Fe-25 at.% Al has been investigated in sulphuric acid [121, 122]. The results proved that the oxide scale not only protected the iron aluminide perfectly against aqueous corrosion, but even self-healing of the scale was observed after long-term immersion. To further elucidate why the oxide scale is so protective, it has been analysed using high-resolution techniques [49, 123]. Grazing incident XRD revealed that the scale consists mainly out of α-Al2O3, with a small fraction of spinel ($FeAl_2O_4$). Investigation of a cross section of the immersed oxide scale by TEM methods revealed its microstructure in detail (Fig. 14). Corrosive attack is limited to the outer layer of the scale, which consists of α-Al_2O_3 + $FeAl_2O_4$. The inner layer is formed of columnar α-Al_2O_3 with few grain boundaries, which inhibit further ingress of the acid to the scale/metal interface (Fig. 14). Compressive stresses, which developed during cooling from pre-oxidation at 1000 °C, are also helpful for “sealing” the grain boundaries [49].

Other activities on iron aluminides and iron-based alloys include critical assessments of the phase equilibria, phase transformations and thermodynamics of the ternary systems Fe–Al–Co [75], Fe–Nb–Ti [124], and Fe–Nb–V [125], a summarizing account of a collaboration with industries on the characterization of the microstructure, corrosion and mechanical behaviour of combustion chamber prototypes for marine engines before and after testing [126], and investigations by electron probe micro analysis (EPMA) to settle whether cementite (Fe_3C) shows a homogeneity range [127].

The importance of iron aluminides as a new class of sustainable materials for CO_2-reduced transportation and energy applications, and the substantial contributions at the MPIE for their development, have been demonstrated in a couple of honourable publications. An invited review on the history, phase diagram and crystal structures, physical and mechanical properties, corrosion behaviour, synthesis, processing and application has been published [32]. A discussion of the role of iron aluminides as inexpensive and easily recyclable alloys for demanding applications was chosen by the Max Planck Society as one of the ‘Highlights from the yearbook of the Max Planck Society 2019’ [128], and there has been a radio Deutschlandfunk report about the group’s work on sustainable iron aluminides [129]. Iron aluminides were also included in a book chapter on ‘Iron-Based Intermetallics’, which in addition dealt with iron silicides, iron-based ferritic superalloys, and iron-based alloys with TCP phases [46]. Finally, a publication contract to edit a book on ‘Ternary Iron Phase Diagrams Relevant for the Application of Iron Aluminides’ has been signed.

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