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# Department of Computational Materials Design (CM)

J. Neugebauer

# **Scientific Objective and Department Structure**

The research activities of the Department of Computational Materials Design are based on three pillars: (i) the development and implementation of advanced ab initio guided multiscale approaches and algorithms, (ii) the use of these techniques to unravel fundamental mechanisms behind materials phenomena and properties, and (iii) the use of these insights to develop novel strategies in materials discovery, synthesis, and design. This unique combination of advanced fundamental theoretical, algorithmic, and software developments with real-world materials science applications allows the department to push the boundaries of materials science questions that can be successfully addressed by ab initio guided modeling. It also provides a solid foundation to cover a wide range of materials systems, such as metallic alloys, semiconductors, magnets, compositionally complex alloys, and electrochemical interfaces, as well as to study properties of real materials, such as the complexity of microstructure defects and their response to reactive environments, such as corrosion or embrittlement phenomena.

The first pillar, the development and implementation of advanced ab initio guided multiscale approaches and algorithms, involves not only the development of novel theoretical or numerical concepts, but also ensures their implementation according to FAIR (Findable, Accessible, Interoperable, and Reusable) principles. A major role in achieving these principles is played by our pyiron Integrated Development Environment (IDE), with a strong focus on materials science simulations. This framework has been systematically developed and extended over the last reporting periods and has become central to collaborative research not only between all research groups within the department, but also for external collaborations. Examples in this reporting period include the generation of new methodologies that exploit exascale computing capabilities to efficiently run complex simulation workflows that combine computer codes specialized for different lengths and time scales, the development of autonomously running workflows to compute complex material properties such as melting temperature, enthalpy and entropy [1], defect phase diagrams [2-8], to run and analyze electrochemical reactions [9,10] or to employ ab initio and machine learning techniques to support the design and analysis of advanced experiments [11-22]. Another line of research has been the development and exploration of computationally efficient surrogate models for ab initio finite temperature calculations. Examples include approaches that allow accurate determination of free energies at finite temperatures, including anharmonic contributions, that do not require statistical sampling

[23,24], or that include nuclear quantum effects but require only classical molecular dynamics simulations [25]. The department's work in these areas has led to hugely improved computational efficiency, rapid prototyping, and vastly improved experimental setups and analysis, providing unprecedented insight into complex material behavior, as discussed below.

Under the second pillar, the Department uses these techniques very successfully to reveal the fundamental mechanisms behind materials phenomena and properties. In many cases, these techniques have allowed us to provide a complementary view to state-of-the-art experiments and to overcome the challenges and limitations of experiments in terms of sample preparation, resolution, or detection of single atomic events [14-18,20-22]. Another prominent example is our study of Mg corrosion, where the development of a fully ab initio setup of an electrochemical interface containing the full complexity of the real system, including explicit water, and a charged, and thermodynamically consistently potentiated interface, allowed us to solve a 150-year-old puzzle related to Mg corrosion. As pointed out in Ref. [10], under anodic (electron-deficient) conditions, Mg dissolves not as a solvated Mg<sup>2+</sup><sub>ag</sub> ion, but as a solvated [Mg<sup>2+</sup>OH<sup>-</sup>]+<sub>ag</sub> complex. This mechanism, which had never been considered before, could be deduced directly from the ab initio molecular dynamics simulation, which nicely illustrates the possibilities of such methodological developments for understanding complex and unimaginable reaction pathways. The discovery of such unknown mechanisms by novel simulation techniques has direct consequences in resolving conflicting experimental observations and in arriving at a unified theoretical framework. In the case of Mg, for example, we have been able to explain why an apparently univalent Mg<sup>+</sup>, ion is observed in coulometric measurements (it is the singly charged [Mg<sup>2+</sup>OH<sup>-</sup>]<sup>+</sup><sub>ad</sub> complex), or why the anodic hydrogen evolution reaction is so violent (because the complex transports away the potentially passivating OH groups).

Another important example is the development of concepts and simulation techniques for metastable defect phase diagrams (see p. 216) by combining the theory of metastable bulk phase diagrams with defect phase diagrams [2,6,8]. Bringing defect phase diagrams to the same level as bulk phase diagrams is critical to provide materials designers with a tool to chemically control defect formation, structure, and properties. The developed methodology, which uses the concept of chemical potentials to link the energetics and concentration of solutes in different bulk and defect phases, provides a fully *ab initio* route to construct such metastable defect phase diagrams. The availability of such novel phase diagrams enabled us to derive fully quantitative strategies for the synthesis of specific defect states. When provided to our experimental collaborators in the SN department (G. Dehm, see p. 181), NG group (C. Scheu, see p. 17), and at RWTH Aachen university, they successfully synthesized and observed with atomic resolution the predicted defect phases, thus confirming the theoretical predictions [8,26]. These examples show again how new and emerging fields in materials science can directly benefit from the systematic advancement and extension of *ab initio* based approaches to ever more complex systems.

Finally, the third pillar revolves around the translation of these insights into novel strategies for materials discovery, synthesis, and design. As outlined in the previous examples, the department's approach is not just to isolate and understand the phenomena, but to use this understanding to provide our experimental collaborators with all the inputs they need to synthesize and design new materials [8,27,28]. The emphasis is on making a real-world impact - developing materials for sustainable and green technologies, energy generation and storage, or developing strategies to prevent corrosion or embrittlement, thereby extending the life and safety of products made from these materials.

To address this broad portfolio of materials systems and methods, the department is organized in five groups: Tilmann Hickel, who heads the Computational Phase Studies group, focuses on the ab initio description of bulk and defect thermodynamics using ab initio methods, as well as on the various aspects of providing an efficient infrastructure for digitalization in materials science. Tilmann Hickel held a joint position of MPI-SusMat and the Federal Institute for Materials Research and Testing (BAM) in Berlin until summer 2023. This joint position was very successful in coordinating and stimulating the cooperation between these institutions and in keeping the pyiron activities and developments coordinated. In the summer of 2023, Tilmann Hickel accepted a full-time position at BAM as Head of the Materials Informatics Department. To provide a permanent and sustainable basis for this collaboration, which is beneficial for both institutions and to coordinate the joint activities on the pyiron developments, he accepted a 10% position at the MPI-SusMat. Part of the ab initio thermodynamics activities carried out in Tilmann Hickel's group will be continued by a new group formed in the CM department. This group, Materials Informatics, led by Jan Janssen, will focus on ab initio thermodynamics as well as on the development of automated tools for exploring large materials data spaces using various machine learning techniques, including large language models. Jan Janssen, who worked at Los Alamos National Laboratory on the development of tools for running complex materials science simulation workflows on exascale computers, and who developed major parts of the pyiron framework in his Ph.D. thesis at our institute, brings the perfect expertise for these challenging tasks.



**Fig. 1:** The CM department at the department retreat at Ebernburg, summer 2023.

Erik Bitzek, who started shortly before the end of the last reporting period in September 2021, successfully established his new group on Microstructure and Mechanics. He has significantly expanded the department's ability to describe large-scale phenomena such as fracture, defect formation, evolution, and kinetics far beyond what can be done with *ab initio* techniques, and has established new links and collaborations with the experimental departments.

Mira Todorova's group on Electrochemistry and Corrosion addresses the various methodological and materialspecific issues related to surfaces and electrochemical interfaces. These research activities, which are closely linked to the GO department, in particular the group of Stefan Wippermann, provide unique ab initio-based approaches and insights into critical degradation phenomena. Christoph Freysoldt's group on Defect Chemistry and Spectroscopy is leading the development of computationally efficient and highly accurate methods for describing the formation of defects and their electronic structure in semiconductors and insulators for both bulk and lower dimensional structures. He also directs and manages all activities related to our highperformance computing cluster, which is at the heart of our computationally intensive research in the department.

These activities are complemented by the Compositionally Complex Alloys project group led by Fritz Körmann. With his team and in close collaboration with the MA department (see p. 161), he has been very successful in exploiting the vast chemical configuration space of such alloys to develop materials with superior mechanical or magnetic properties.

During the reporting period, the department's ability to explore and navigate large and complex chemical and structural configuration spaces has grown tremendously. The ability to explore large configuration spaces is related less to improved computational resources than to systematic method development. On the one hand, we started early to adopt, extend and use tools and algorithms from the machine learning community. On the other hand, our pyiron framework provided a solid foundation for the largely autonomous execution of complex workflows integrating advanced electronic structure codes, atomistic molecular dynamics simulations, ther modynamic calculations and machine learning. While in the previous reporting period our machine learning activities were mainly used to coarse-grain the computationally intensive *ab initio* calculations, e.g. by constructing on- and off-lattice interatomic potentials, in the current reporting period we used a much broader arsenal of techniques. In particular, advances in non-numerical machine learning approaches that make direct use of textual and contextual information have opened up new possibilities [19,29]. Close collaboration with other departments was also critical to the successful discovery of new materials [3,27]. They not only provided experimental validation of predicted results, but were often directly involved in motivating research topics and in the active learning loop.

These techniques have been successfully applied to a wide range of applications, from exploring chemical compositions for hard magnets that eliminate economically undesirable elements [28] to exploiting the large chemical configuration space of compositionally complex alloys [27,30]. The latter study, published in Science, demonstrated the power of combining a variety of advanced experimental, data-driven, and computational approaches, combining material synthesis, analysis, experimental databases, various machine learning techniques, and ab initio calculations of key descriptors in an active learning loop. This combination led to the discovery of novel High Entropy Alloy (HEA)-based Invar alloys that significantly outperformed previous human-based design efforts. These examples nicely illustrate the opportunities and benefits of the close coupling of advanced experimental and theoretical techniques at MPI-SusMat. This holistic approach, which has been systematically developed at our institute over the past few years, allows us to exploit the strengths of complementary techniques while avoiding their weaknesses in terms of resolution, cost (e.g. for sample preparation), computational complexity or accuracy, and to adapt well to machine learning approaches in terms of active learning and data reduction of the most expensive steps.

The versatility and maturity machine learning approaches have achieved in describing complex materials phenomena has been also demonstrated in a project related to identifying and predicting the corrosion rate as a function of alloy composition and electrochemical environment [13,19]. These studies, which were based on large experimental databases consisting of several thousand entries, not only used numerical data but showed that including text, describing the experimental setup, in the machine learning process improves the predictive power. Further examples are described in the group reports and highlight articles (see p. 232,234,238).

The broad methodological expertise of the department, with many methodological advances coming from the members of the department, together with the wide range of materials, provided an excellent basis to address the new topics and scientific challenges related to the new direction of the institute towards sustainable materials. In fact, many of the scientific issues related to the new direction, such as electrochemical processes for energy conversion, formation and properties of oxides, or materials for energy saving applications, have been systematically advanced by the department over the last decade.

Examples are the development of powerful, fully ab initio based theoretical methods for the description of electrochemical interfaces (see p. 79, 212), materials exhibiting spontaneous polarization of group III-nitrides for energy efficient solid state optoelectronics, for a new generation of power electronic devices needed e.g. in energy converters for regenerative power generation, the formation of heterointerfaces exhibiting a two-dimensional electron gas [31], e.g. for sensing or understanding the formation of oxide films under corrosive environments. Christoph Freysoldt's group has the mathematical and methodological expertise for oxides to describe the formation energy and electronic structure of their intrinsic point defects such as vacancies, interstitials or antisites with extreme precision and high computational efficiency, even in small supercells. In the current reporting period, this methodological expertise has been extended from periodic bulk crystalline systems to low-dimensional structures such as surfaces or 2D materials [32] and polaronic systems [33].

Having this expertise from the Todorova and Freysoldt groups in the department allowed us to quickly get started on topics related to carbon-free oxide reduction, such as replacing carbon with an H<sub>2</sub> gas or plasma as a reducing agent. In contrast to carbon reduction, even the basic steps of oxide reduction are unknown. Using our expertise in oxides and in close collaboration with the experimental activities in the MA department (see p. 161), we have systematically studied and analyzed various ab initio techniques to accurately describe the different bulk oxide phases, surfaces and point defects and their interaction with hydrogen. The focus is on iron and its oxides, since this material system is highly relevant for green steel production. Strong electron localization, spin moments and interactions make the description of these oxides challenging by conventional DFT methods, often requiring us to develop methods and approaches that go beyond the conventional.

The department is also at the forefront of the development and provision of the infrastructure needed for digitization in materials science. Tilmann Hickel leads and coordinates these developments in a concerted effort both in his groups at the Federal Institute for Materials Research and Testing (BAM) in Berlin and at the MPI-SusMat. Using the pyiron framework, he contributes the department's expertise in providing and developing an infrastructure for the development and operation of complex workflows as a board member in the two major national infrastructure initiatives: The National Research Data Infrastructure (NFDI) consortium MatWerk (see p. 86), focused on the academic research community, and the German Federal Ministry of Education and Research (BMBF) funded Platform MaterialDigital (PMD) (see p. 88), focused on industry. These activities are strongly supported by the group of Jan Janssen, who actively stimulates and directs the development of pyiron in all

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its facets. The high esteem in which the members of the department are held in these large-scale digitization initiatives can also be seen in the fact that another CM group leader - Erik Bitzek - is co-spokesman of the NFDI-MatWerk, where he represents the task area Material Data Infrastructure.

Many of the breakthroughs achieved in method development (see p. 212, 216, 222, 234) [23, 34], application (see p. 218, 208, 228) [11,12,35] or design (see p. 226) [19,21,29] have only been possible by combining the individual expertise developed by the groups in the department. The pyiron framework has become an efficient and versatile link that connects the different development activities of the groups and provides them with a collaborative platform that allows them to work together on new methods or to share them easily. The pyiron platform has also helped tremendously in collaborating with internal and external partners. Examples include work on ab initio thermodynamics [1,35-37], defect phase diagrams [6,8,26], machine learning potentials [34,38-40], electrochemistry [9,10,41], material design [27,28], or high entropy alloys [30], to name a few.



**Fig. 2:** (left) Prof. Neugebauer in front of the banner of the MMM11 conference, holding the ISMM distinguished career award he has just received; (right) Dr. Todorova holding the certificate for the Alexander Kuznetsov Award, which she has just received from Prof. Dr. Katharina Krischer, President of the International Society of Electrochemistry.

The important scientific breakthroughs achieved by members of the CM Department have been recognized by the international community. Several prestigious prizes have been awarded (see p. 233):

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Mira Todorova's outstanding contributions to theoretical electrochemistry have been recognized with the Alexander Kuznetsov Prize for Theoretical Electrochemistry 2023. She received the award during the 75<sup>th</sup> Annual Meeting of the International Society of Electrochemistry (ISE) in Montreal. Canada 2024. Christoph Frevsoldt was awarded the J. H. Block Lecture at the APT&M '23 conference and elected to the Steering Committee of the International Field Emission Society in recognition of his contributions to the theoretical understanding of atom probe tomography (APT). Jörg Neugebauer received the prestigious ISMM Distinguished Career Award for his work on first principles-based multiscale materials design that has enabled precise and efficient computations of real-world materials properties and processes. The award, which recognizes an individual who has advanced the field of materials modeling through innovative, career-long research contributions, was presented at the

11<sup>th</sup> Multiscale Materials Modeling (MMM) meeting in Prague, Czech Republic. Jan Janssen, who recently started as a group leader in the CM department, and his team won the first prize at the Large Language Model (LLM) Hackathon for Applications in Materials and Chemistry with their interface for LLMs to compute fundamental atomistic material properties using pyiron, demonstrating well how the methodological advances of the pyiron framework are well suited to integrate recent developments such as Large Language Models.

Also, the more junior scientists received prestigious awards: Jing Yang (in 2023) and Daria Smirnova (in 2024) were awarded with the SignUp! Career Development Programme, and B. Eggle-Sievers and S. Ghosh received best poster prizes at international conferences. Several members of the department (Ali Tehranchi and Christoph Freysoldt) were recognized as outstanding reviewer/ referee from key journals in our field (Acta Materialia, Scripta Materialia, Physical Review).

The high visibility and impact of the scientific work performed by members of the department on the materials and modeling community has resulted in several invited reviews on recent methodological developments and new research directions in leading scientific journals, covering areas such as compositionally complex alloys [29,42], ab initio description of electrochemical systems [43], large data applications in materials science [44], or the application of Large Language Models (LLMs) in materials science [45]. The fact that the department is at the forefront of materials modeling in many areas also makes it highly attractive to external research experts. Currently, the department hosts three international experts who have received prestigious AvH awards (Bin Wang from the University of Oklahoma - AvH Bessel Award and Jing Yang and Baptiste Bienvenue - Postdoctoral Humboldt Research Fellowships).



Fig. 3: Group picture taken during the ADIS2023 workshop "Digitalization and Workflows" at Ringberg Castle.

To foster collaboration with leading international experts, members of the department have been actively involved in initiating and organizing international workshops and symposia (see p. 262). These include workshops initiated by the CM Department, such as ADIS (Ab Initio Description of Iron and Steel) organized by Tilmann Hickel or the Ringberg Workshops on Surface and Electrochemistry phenomena organized by Mira Todorova and Christoph Freysoldt. Besides many classical workshops and symposia with talks (e.g. at the meetings of the German Physical Society (DPG) or within the program of the Institute for Pure and Applied Mathematics (IPAM) at the University of California, the pyiron framework proved to be an extremely effective tool for organizing highly interactive hands-on workshops in a hackathon-like format. Examples are tutorials on workflows in materials science simulations at the DPG Spring Meetings in 2023 and 2024, or multi-day hackathon workshops on the construction and application of machine learning capabilities using pyiron as a workflow manager (Reisensburg 2022, Bochum 2023). Based on recent research findings in the department, Jörg Neugebauer proposed as lead organizer a long-term three-month IPAM program on the mathematical description of stochastic fluctuations at electrochemical interfaces, which was granted for fall 2025.

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

# **Research groups**

# Microstructure and Mechanics (E. Bitzek)

The mechanical properties of materials are intricately connected to their microstructure, encompassing the full spectrum of crystal defects. The research group "Microstructure and Mechanics" is at the forefront of exploring these elementary defects of the crystalline lattice-such as dislocations, cracks, interfaces, and point defectsand elucidating how their interactions and self-organization dictate critical material properties, including strength, ductility, hardness, and fracture toughness. This research is vital for understanding materials' behavior under various loading conditions such as fatigue, creep, friction, and wear. To advance this understanding, the group employs large-scale atomistic simulations involving up to billions of atoms, enabling unprecedented insight into defect properties and the mechanisms governing defect-defect interactions. Such simulations are important for translating experimentally motivated challenges into detailed atomistic understanding. The group's work is known for its innovative approaches to sample generation and defect analysis and close collaboration with experimental scientists.

Established with Erik Bitzek's transition from FAU Erlangen-Nürnberg to the institute in September 2021, the group – which maintained until July 2024 a presence at FAU -has strategically positioned itself within the MPI-SusMat, where it complements and enhances the expertise of the CM department. Their research contributes significantly to interdepartmental projects such as (see p. 80, 82, 86, 101, 107, 224).

As the results of large-scale atomistic simulations critically depend on the quality of the interatomic potentials used, the group is also directly involved in developing such potentials [34,46]. These methods nowadays allow the large-scale simulation of defect-defect interactions and micromechanical tests. Therefore, the Microstructure and Mechanics group collaborates closely with experimental groups [47,48], in particular, the group of James Best at MPI-SusMat [49,50], including in the development of new experimental methods [51]. A major focus of the group's work lies in advancing our understanding of fracture mechanics, particularly how microstructural features influence crack propagation. This research is highlighted in the sections on the ERC project "Microscopic Origins of Fracture Toughness" (see p. 56) and the collaborative research on "Fracture across Scales" (see p. 224). Their findings are foundational, offering new perspectives on how defects within a material's microstructure can be manipulated to enhance fracture resistance, thus paving the way for the development of tougher, more reliable materials.

Another cornerstone of the group's research is the study of dislocation properties, including dislocation nucleation, motion, and interaction with defects, like other dislocations, cracks, and interfaces. Here, one area of current interest is the behavior of dislocations in compositionally complex single-phase alloys (also referred to as high entropy alloys or HEAs). Using atomistic simulations in collaboration with Michael Zaiser (FAU), we could show that in such alloys, metastable dislocation configurations are not associated with local obstacles but with larger-scale compositional fluctuations along the cores of partial dislocations. These fluctuations, rather than the composition across the stacking fault, control dislocation pinning. The ability of dissociated dislocations to adapt their local stacking fault width and thereby minimize the forces acting on both partials provides an additional internal degree of freedom. Consequently, partial dislocations can be pinned independently, resulting in many metastable states and complex behavior. For example, the stacking fault width becomes history-dependent. The degree to which the partial dislocations can arrange themselves according to the local fluctuations depends on the dislocation length. The hardening contribution of HEAs, therefore, becomes size dependent. This implies that different strengthening mechanisms in concentrated solid solutions are not merely additive but may behave super-additively, as we could demonstrate using voids as obstacles, see Fig. 4. [52,53]. These findings enabled realistic modelling of partial dislocation pinning in dislocation dynamics simulations and opened up novel pathways for enhancing the mechanical performance of concentrated solid solutions.

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Fig. 4: Critical resolved shear stress (CRSS) needed to overcome obstacles is shown as a function of the periodic void spacing. (a) with and without a void present, showing the size-dependence of the CRSS even without obstacles. (b) Fits using the BKS (Bacon, Kocks and Scattergood) equation, with the green curve using an additive superposition, i.e., best-fit constant C value, while the red curve uses a synergistic superposition [53].

The properties of dislocations in Laves phases were investigated within the context of the SFB1394 (see p. 82) [54-56]. Detailed analysis atomistic simulations showed for the first time that the leading and trailing 30° Synchro-Shockley partial dislocations in C14 CaMg, and C15 CaAl<sub>2</sub> Laves phases have distinct core structures and energies, even though they are of the same character. Consequently, they display different propagation mechanisms in nudged-elastic band calculations: kink pair formation and propagation vs. nonsequential atomic shuffling, shear straining, and atomic rearrangement. Both mechanisms involve the creation of point defects and are thus strongly dependent on the chemical composition. Their different thermal activation energies furthermore point towards a direction dependence in the plastic deformation of Laves phases.

Dislocation processes can nowadays be studied directly using in-situ nanomechanical tests within transmission electron microscopes (TEM). These experiments, however, lack the time resolution to investigate the detailed mechanisms involved in dislocation nucleation and dislocation-dislocation interactions. Ultra large-scale simulations can be used to study these details in atomicscale digital twins while allowing for well-controlled variations, e.g., in system size. One example of such a study with half a billion atoms is shown in Fig. 5. Electron tomography (ET) on a single-crystalline, defect-free nanoporous gold pillar was used to create an identicallysized atomistic sample. The pillar and the atomic sample were compressed, unloaded, and analyzed. In addition, geometrically constructed samples with the same porosity and average strut size but different topology and down-sized samples were studied. Interestingly, only the digital twin of the original pillar showed the same flow stress and the same developing microstructure as the experiment. This highlights, both the importance of size and topology (scaled genus density, distribution of strut sizes) on the deformation mechanisms. In particular, this study showed for the first time the formation of stacking fault tetrahedra in atomistic simulations of nanoporous gold. The atomic-scale formation mechanism of SFTs (Stacking Fault Tetrahedra/ Tetrahedron) and small-angle grain boundaries were identified, and their existence was rationalized by a new size- and orientation-dependent model for dislocation nucleation [48].

Recently, the Microstructure and Mechanics group has also moved into the study of amorphous materials, like (sodium-)silicate or metaphosphate glasses [57-59]. Glasses are typically thought of as the archetypical brittle material. However, it is well known that glasses can deform plastically under uni- or multiaxial compression. Using large-scale molecular dynamics simulations and applying analysis methods from metallurgy like stereographic projections, the group tries to uncover the atomic-scale mechanisms preceding fracture. The central goal is to derive new toughening processes based on targeted pre-deformation and to study how these toughening mechanisms interact with the usual chemical routes to improve the mechanical properties of glasses. In a foundational study, it could be shown that silica glass under load displays reversible, transient anisotropy, while after unloading they show persistent anisotropy - and that both types of anisotropy have different structural origins. Under compression, the ring normals orient themselves parallel to the compression axis. During this deformation, bonds orthogonal to the compression axis can break and reform shorter bonds along the compression axis. Upon unloading, these bonds are maintained and under tensile strain, which influences further deformation, see Fig. 6. Interestingly, for metaphosphate glasses, which show a 1D chain structure instead of the 3D random network structure of silica glass, transient and persistent anisotropy have the same structural origin, namely, the reorientation of the chains. The persistent and especially the transient anisotropy is of fundamental importance during the deformation and fracture of oxide glasses as it constitutes the initial response of the glass network to mechanical load and thereby defines all subsequent mechanical reactions.



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**Fig. 5:** Top: sketch of the correlative approach to study the deformation of nanoporous Au (NPG: nanoporous gold) by 3D microscopy (nano-CT, electron tomography ET), MD and FEM. Bottom: a) and b) show the same section of the de-formed NPG in TEM and MD; c) shows the full simulated part of the NPG highlighting the characteristic defects: small angle grain boundaries, stacking fault tetrahedra and micro-twins [48].

Prof. Bitzek is furthermore strongly involved in the German research data management initiative NFDI-MatWerk, where he is a co-spokesperson representing the task area Materials data infrastructure and is actively involved in the development of reference datasets, planning of the rollout process and organizing RDM workshops. He is also the scientific coordinator of the International Max Planck Research School IMPRS SusMet (see p. 80) and member of the editorial boards of International Materials Reviews and the Journal of Molecular Modeling. In May 2024 he was elected to serve on the review board for materials science and engineering of the German Science Foundation DFG.





**Fig. 6**: Top: small segments from a large-scale MD simulation of silica glass. Before uniaxial compression (left), the rings are randomly oriented. During compression (middle), the rings orient themselves with their axis parallel to the compression direction, and orthogonal bonds are preferably broken and replaced by bonds along the axis. This structure remains upon unloading, leading to persistent anisotropy (right) [57].

# Computational Phase Studies (T. Hickel)

The group "Computational Phase Studies" (CPS) is devoted to the physics and computation of (meta)stable thermodynamic phases in metals as well as transitions between them. While the major vision was in the past on the development of materials scientific concepts required for an *ab initio* based prediction of thermodynamic bulk and defect phase diagrams, the implementation of corresponding workflows became increasingly more important in recent years. This strengthens the goal to provide access to many technologically relevant properties and processes in metals. The main research fields in this context are:

- The continued efforts to push *ab initio* thermodynamics to its limits, increasingly relying on machine-learning potentials as an excellent chance to combine precision and efficiency.
- The extension of *ab initio* thermodynamics to extended defects, such as grain boundaries, stacking faults and interfaces, is meanwhile established in the group.
- There is a variety of applications for which the interplay of hydrogen and bulk or defect phase stabilities is central for the group.
- The exploration of chemical trends is used to design novel materials.
- The development of generalized workflow solutions that make the simulations in the above-mentioned fields transparent and reproducible.

The group's activities are also marked by the fact that its head, T. Hickel, has taken over the division head position of Materials Informatics at the Federal Institute of Materials Research and Testing (BAM). This began in 2021 as a second employment but has been his main position since 2023, giving him only a limited amount of time for tasks that are specifically dedicated to MPI-SusMat. The

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double position is still possible and meaningful, due to the mutual and global benefits that arise from the cooperation of these institutions.

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Such a benefit is particularly obvious in the digitalization strategies pushed forward by both institutions in two joint projects: NFDI-MatWerk (see p. 86) is the consortium within the national research data initiative that develops the digital standards for the Materials Science and Engineering (MSE) community. The Platform MaterialDigital (see p. 88) provides prototypical solutions for the exchange of materials data between project partners taking industrial demands into account. In both cases, innovative ideas of MPI-SusMat and the sustainability and reach of BAM form an important combination for the success of the digitalization missions. The Integrated Development Environment (IDE) pyiron (see p.77) developed at MPI-SusMat forms a cornerstone in these developments, as it considers research data and workflows [60-62] to generate them as a unity. The environment is already unique in the way it simplifies and structures the research of materials scientists, but is still constantly adapted to meet the demands of the MSE community both in NFDI-MatWerk (S. Menon, M. Bruns) and MaterialDigital (O. Waseda, H. Mai). Along these lines, two development directions are strongly linked to the activities of the CPS group.

The increase in the interoperability of the employed steps and research software is one strong tendency in pyiron. It is achieved by enforcing a modular structure in the Jupyter notebooks of pyiron. This is achieved by associating with every step of a workflow a new node with well-defined in and output, which are described by an ontology. Due to this structure and in particular due to the semantic representation based on knowledge graphs, a new combination of workflow steps and a replacement of one step by another becomes straightforward. This gives access to multiscale simulations, which are important for the work in the group. In several projects, there is experience with coupling *ab initio* simulations with finite element simulations (see p. 104), with the crystal-plasticity code DAMASK (see p. 240) or with phase-field simulations [63].

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**Fig. 7:** Phase diagram of hydrides in a FeCr20 alloy, based on the formation energy per metal atom (top) and in the external indentation load -- chemical potential space (bottom).  $C_b$  is the bulk hydrogen concentration at 300 K and  $\Delta\mu_H$  the hydrogen chemical potential referenced to an  $H_2$  molecule. Details can be found in (see p. 204) and Ref. [8].

The thermodynamics of defects is meanwhile an established research direction in the CPS group, for which these thermodynamics concepts are used to achieve a new level of understanding the microstructure-related performance of materials. These activities are strongly linked to the SFB1394 (see p. 82) [2], but now also yield many ground-breaking insights in collaborations with other partners [67]. The concept of defect-phase diagrams opens a new route of research involving fundamental considerations on meta-stability [8] and competing bulk phases (P. Mathews) [68], which were the result of long-standing scientific debates with theoretical and experimental colleagues. A large spectrum of defects has now become thermodynamically accessible in various material systems, including vacancies in intermetallic phases [3], interfaces in Al allovs [69], and stacking faults in hydrides [7].

The investigation of hydrogen in materials is a specific field, where the defect thermodynamics gets a strong link to applications and current efforts for more sustainable energy resources. One of the highlights in this context is the identification of the central role of impurity segregation to grain boundaries for the embrittlement effect in Al alloys [67]. Another highlight is a suggested strategy to exploit the stress fields of defects such as microcracks in order to trigger the formation of local hydrides in Al alloys [5]. The formation of hydrides in the vicinity of de-



Fig. 8: Extension of the pyiron platform as scientific foundation model combining literature research, empirical models, CALPHAD modelling and atomistic simulation as a central agent to accelerate the discovery of sustainable materials.

fects has been further confirmed in a collaborative work with the SN department (see p. 181) on nanoindentation of FeCr alloys [8] (see Fig. 7).

The methods and insights achieved in the group are further used to explore chemical trends and therewith design a broad spectrum of novel materials. In the context of hydrogen, in particular the role of alloying elements in the stabilization of carbides and their relevance as trapping centers for hydrogen has been explored [70]. The stabilization of intermetallic phases by alloying elements has also been analyzed in Ni-based superalloys [71]. In a similar way, we have continued our efforts to find the best chemical composition that stabilizes permanent magnets [28]. However, the increase of chemical complexity is still challenging the computational concepts developed in the group and the department. For example, a lot of efforts were necessary to extend the ab initio prediction of melting temperatures from unary to binary materials [1]. The group will continue its efforts in this direction, combining novel physical and computational approaches as outlined above.

# Materials Informatics (J. Janssen)

In 2023 J. Janssen, who completed his PhD at the MPI-SusMat in 2021, returned to the institute to lead the Materials Informatics (MI) group (see p. 47) after a Postdoc at Los Alamos National Laboratory. With his newly acguired expertise in the fitting of machine learning interatomic potentials (MLIP) based on the development of the FITSNAP [72] code and the experience in Exascale computing as part of the Exascale Atomistic Capability for Accuracy, Length, and Time (EXAALT) project, he bridges the gap between innovation in computer science and their application to materials science. From the beginning the MI group has been involved in the continuous method development of methodologies for ab initio thermodynamics (see p. 66). Beyond the CM department, the group closely collaborates with the MA department to combine insights from experiment, theoretical modelling, simulation, and more recently, data-driven and machine-learned approaches in Materials Acceleration

Platforms (MAP) (see p. 232). Both of these activities are based on the pyiron workflow framework which was initially developed during the PhD of J. Janssen [73]. In April 2024 H. Gaafer joined the MI group as a PhD student with a focus on improving the computational efficiency of MLIPs to enable a more direct comparison to experiments.

The group aims to address the demand for new materials with machine learning. This applies especially to the design of new sustainable materials which come with many additional constraints like availability of scrap components, ability to recycle the material, or being a non-toxic material. For this application the types of machine-learning range from MLIPs, over Bayesian approaches as applied in MAPs to more recently Large Language Models (LLM). With the later J. Janssen and his team of international collaborators won the "2nd LLM Hackathon for Applications in Materials and Chemistry" with their interface for LLMs to calculate atomistic material properties using pyiron. This development is in close collaboration with the Center for Scientific Foundation Models at the University of Michigan and MPI-SusMat. K. Limbasiya joined the MI group as a student assistant in August 2023 to develop foundation models for sustainable materials.

To achieve this level of automation and to handle the increasing technical complexity of simulation workflows a workflow framework has to support both the rapid prototyping and up-scaling of the same workflows. J. Janssen continues to lead the pyiron development (see p. 77) to address this challenge. Especially with the recent transition from an object-oriented to a functional approach, pyiron not only achieved the scalability required to execute workflows on the first Exascale Computer - Frontier at Oak Ridge National Laboratory - but at the same time this transition simplified the user interface. While previously optimal efficiency and user-friendly interface were accepted as contradictions, the new pyiron version highlights that efficient workflows do not have to be complex. These current prototypes provide a preview of the up-coming next iteration of the pyiron workflow framework as illustrated in Fig. 8 above.

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Finally, with the transition of T. Hickel and the Computational Phase Studies group from the MPI-SusMat to the BAM Federal Institute of Materials Science and Testing, the MI group continues the development of methods for *ab initio* thermodynamics. This includes the involvement of J. Janssen in the CRC 1394 (see p. 82).

# Electrochemistry and Corrosion (M. Todorova)

The work of the Electrochemistry and Corrosion Group focuses on understanding how interactions with the environment affect and modify materials and their properties. As the longevity of materials and electrochemical processes are essential cornerstones of a sustainable future, the group's strong focus on corrosion and electrochemical solid/liquid interfaces remains central. These topics are complemented by related questions concerned with modifying or controlling materials by external stimuli, such as the reduction of iron ores by hydrogen, or by internal ones, such as the spontaneous polarization common in wurtzite materials. The fruitful collaboration with S. Wippermann (GO department (see p. 143)) & University of Marburg) and C. Freysoldt (CM) on the development of methods to solve problems related to electrochemical solid/liquid interfaces continues (see p. 79, 212). Collaborations with colleagues from the experimental departments - B. Gault and X. Zhou (MA), T. Scheu (NG) and M. Rohwerder (GO) and ICAMS (group of R. Drautz) are also ongoing.

The corroding Mg system continues to provide fascinating mechanistic insights and pushes us to develop methods that allow us to reconcile experimental observations. The application of the thermopotentiostat to the study of Mg dissolution during corrosion under anodic conditions has allowed us to shed light on an ongoing and hotly debated issue in the experimental literature concerning the existence of a univalent Mg ion. We show [10] that this ion, which has been invoked to explain the observed amount of Mg exceeding coulometric expectations, is likely to be a  $[Mg^{2+}OH]^+_{aq}$  complex. The formation of this complex underlies the anomalous hydrogen evolution reaction observed during the anodic corrosion of Mg and naturally explains the absence of a protective oxide/hydroxide layer typically found under anodic/oxidizing conditions.

To study the early stages of MgCa corrosion, we teamed

up with our experimental colleagues from the MA (see p.

161) and SN (see p. 181) departments who used cryo-at-

om probe tomography, transmission-electron microsco-

py and spectroscopy. MgCa alloys, which are potential

candidates for biodegradable implants, show the forma-

tion of an inward growing intermediate corrosion layer

consisting mainly of monovalent Mg(OH), instead of the

expected MgO or the commonly observed Mg(OH)<sub>2</sub>. Our

calculated Pourbaix diagram shows that the Mg(OH)

structure is only metastable, but may occur for kinetic/

epitaxial reasons. An analysis of its electronic structure

furthermore shows, that while the stoichiometry of the

Mg(OH) phase is unexpected, its bonding is stronger



**Fig. 9:** Molecular dynamic trajectory for a  $Mg(1 \ 2 \ -3 \ 15)/H_2O$  interface. The trajectories of the water molecules trajectories are not shown, of the Mg atoms (yellow balls in the inserted snapshots) are shown in grey. The trajectory of the dissolving kink Mg atom (whitish ball in the snapshots) is shown in red. After about 12 ps the Mg kink atom is ionized and solvated, but remains bound to the surface via an OH<sup>-</sup> group. (Adapted from [10,74]) (see p. 212).

compared to  $Mg(OH)_{2^{1}}$  due to the appearance of a metallic state as a consequence of the partial occupation of the Mg  $sp^{3}$ -hybrides [75].

Continuing the studies of Mg containing a solid solution of Ca and Al as part of our work within the CRC1934 (see p. 82) we found a qualitatively different behavior of these two alloying elements in terms of their segregation to the surface. Al shows a slight preference to segregate to the sub-surface region of Mg(0001), i.e. 2-3 layers below the surface layer. This is due to its smaller size, which does not disturb the Mg lattice significantly and its higher surface energy. As a consequence of this preference and because the incorporation of Al point defects into the MgO and Mg(OH)<sub>2</sub> lattices is unfavorable, as seen in our calculations, Al accumulates at the interface between the metal and the inward growing oxide scale forming in corrosive environments, as observed in the experiment. [76].

Calcium, which has a larger atomic radius than Mg and has a lower surface energy, behaves quite differently. It shows a strong tendency to segregate to the Mg(0001) surface and forms an ordered surface structure at 1/3 ML (monolayer) coverage, where 1/3 of the surface Mg atoms are substituted by Ca. Using our density functional theory (DFT) data to fit a cluster expansion, we were able to rapidly scan a continuous range of surface coverages and construct a convex hull for the formed surface structures. in analogy to the commonly used approach for bulk systems. We observe a distinctly lower energy for the ordered 1/3 ML Ca@Mg(0001) structure, which allowed us to identify the observed energy gap to the continuum of disordered structures as a clear signature of a defect phase [6]. We observed a similar energy gap for Nb substitution at Ni(111) surfaces, again at a 1/3 ML coverage. However, the surface phase diagram of Ni-Nb showed that the 1/3 ML phase becomes dominant only in the range of Nb chemical potentials, where the Nb<sub>2</sub>Ni phase is stable, rendering the 1/3 ML coverage phase only metastable. We therefore conclude, that a thermodynamically stable defect (surface) phase is present in a system if (i) it exhibits an energy gap to the continuum of related structures (e.g. all possible surfaces structures in the studied coverage range) and (ii) does not fall within the chemical potential range of a competing intermetallic phase [41].

Using our analysis and insights into the formation of surface phases in these metallic systems, we developed an analytical thermodynamic model to describe defect phase transformations. The statistical phase evaluation approach (SPEA), as we coined it, assumes a Boltzmann distribution of finite size phase fractions and calculates their statistical mean [41]. SPEA correctly predicts the surface order/disorder transition and the coexistence of the 1/3 ML and the disorder phase at a fraction of the computational costs required to obtain this information using Monte Carlo (MC) calculations. Furthermore, comparison with the commonly used CALPHAD sub-lattice model reveals, that SPEA can be used as a highly efficient substitute for modelling defect phase transitions.

When constructing phase diagrams for the Mg-Ca and Mg-Al surfaces in an aqueous environment, we used an implicit solvent approach [6]. Implicit solvents describe the aqueous electrolyte only approximately, and in their most commonly used form, through its screening properties. A critical assumption behind this approach is that the interface energies needed to construct the defect phase diagrams are not altered by replacing an explicit solvent with an implicit one. However, this assumption has not been rigorously demonstrated. We, therefore, constructed defect phase diagrams using the same three surface structures, but computed once when they are interfaced with an explicit solvent via *ab initio* molecular dynamics (AIMD) calculations and once when interfaced with an implicit solvent. The obtained defect phase diagrams showed that it is necessary to pay special attention to the parameterization of the implicit solvent. We identified the density at which the implicit solvent is switched on as a critical parameter that had to be adjusted to match the experimental solvation energies for the relevant ions (Mg<sup>2+</sup> and Ca2+ and). After this adjustment, the defect phase diagrams obtained by using explicit and implicit solvents became almost identical, enabling us to provide guidelines as to when we can expect an implicit solvent to be a suitable substitute for a full-fledged AIMD calculation [77].

All calculations of the Mg-Ca system were carried out by J. Yang, who is a postdoctoral researcher in the group. In 2023 J. Yang was selected to participate in the (competitive) Max-Planck SignUp! programme, which aims to prepare promising young women scientist for a career in academia or industry. She was also awarded an Alexander von Humbold (AvH) postdoctoral fellowship, which started in 2024.

Calculations for the Ni-Nb system are performed by A. Abdelkawy, a Ph.D. student in the IMPRS SusMet Graduate School (see p. 80), who aims to understand the initial stages of pitting corrosion in Ni superalloys. As part of his Ph.D. project, A. Abdelkawy has also developed an



**Fig. 10:** Side view of a Mg (0001) surface alloyed with Ca (respective top view shown as inset) interfaced with explicit water (left) and implicit solvent (right). The interface phase diagrams calculated using these two approaches (shown as inset) differ, before the implicit solvent parameters are adjusted. The implicit solvent picture nicely shows the bound charge density corresponding to the depicted structure (right). (Journal cover picture for Ref. [77])

approach to map the potential energy surface (PES) using symmetrized plane waves. Interestingly, the application of this method to H in iron oxides revealed that the commonly used DFT+U approaches to treat this system do not provide sufficient control over its magnetic structure. As a consequence, we have focused our attention first on developing a methodology that will provide us with the necessary control to accurately describe the magnetic structure of iron oxides. This question is being pursued by H. Chen under the joint supervision of C. Freysoldt and M. Todorova.

To complement the experimental work on iron ore reduction carried out at the Institute, we are also pursuing a second line of research. B. Bienvenu, a postdoctoral researcher in the group, who has recently been awarded an AvH postdoctoral fellowship starting in 2025, is developing, in collaboration with the group of R. Drautz (ICAMS), atomic cluster expansion (ACE) potentials for the Fe-O system, capable of describing both the metal and oxide phases of Fe. The already fitted ACE potential [39] appears to be quite robust and has already provided fascinating insights into the reduction process of iron ores to iron (see p. 208). We are currently extending this potential to include hydrogen.

S. Surendral completed his work on H at the Pt(111)/water interface by developing a highly efficient scheme to compute laterally resolved free energy surfaces (FES) and spectral signatures of specifically adsorbed ions on electrode surfaces from their AIMD trajectories by exploiting surface symmetries [9]. These studies complement our previous work on the influence of explicit water on the properties of electrochemical interfaces. While key electrochemical quantities such as the electrode potential are highly sensitive to the presence of water molecules, the effect on energetic properties such as the adsorption energy is largely negligible. For quantities such as FES or vibrational spectra, water turns out to be a mere spectator with a very limited impact on these properties [9].

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Based on these insights we expect water to play a more prominent role in the electrochemical reactions that take place on the Au surface. This system is studied by S. H. Mattoso in collaboration with K. Tschulik's group (see p. 26). S. Mattoso, a PhD jointly supervised by S. Wippermann and M. Todorova, is also pursuing the development of a hybrid QM/MM approach to solvation, which should, for example, increase the accuracy of calculated interface energies needed for the construction of phase diagrams compared to implicit solvent calculations. We furthermore work on developing a fully solvated electrode approach, which should circumvent the significant reduction in the electric field strength reaching the interface due to the presence of a hydrophobic gap between the computational Ne-electrode and water, and allow realistically strong fields to be applied to it.

Recognising that electron transfer reactions are central to electrochemical processes, Z. Wang, a postdoctoral researcher in the group, who was until recently funded by an FP-RESOMUS fellowship, focused on identifying reaction coordinates suitable for ab initio and atomistic calculations that would allow us to use Marcus theory. Inspired by semiconductor defect chemistry approaches, we identified the ion charge as an efficient reaction coordinate to obtain "Marcus parabolas". Our developed methodology allows us to quantify the free energy of the reaction barriers and the analysis of the solvation shell evolving along the Marcus parabola path reveals the characteristic features of the transition state geometry. These geometries can be efficiently analyzed using the SolShell python analysis tool (https://github.com/yuyuanjingxuan/pyiron\_solshell) developed by Z. Wang.

S. Yoo concluded his work on materials exhibiting spontaneous polarization by applying our previously developed and reported method for correctly describing slabs of such materials, to identify the microscopic origin of polarization charges at GaN/(Al,Ga)N interfaces [31]. In addition, the group has been involved in the writing of two review articles - one on defect phase diagrams [2] and another focusing on achieving potential control in *ab initio* calculations [43].

Finally, we would like to mention the group's weekly electrochemistry hackathons, where we test ideas, develop analysis tools and work on integrating them into pyiron. Recently, we have used the hackathons to work on integrating our thermopotentiostat approach into the official VASP release to make it available to the community. For this, we utilize the py4vasp tool, in close collaboration with the VASP developers. We also continue to organize workshops focusing on different aspects of modelling electrochemical interfaces, with the last workshop in the series being held in 2022 and the next one taking place in 2025.

# Defect Chemistry and Spectroscopy (C. Freysoldt)

The group "Defect Chemistry and Spectroscopy" works on atomic-scale simulations of electrical charging phe-

nomena by means of *ab initio* methods, and develops state-of-the-art methods and concepts for this purpose. Additionally, the group is active in machine learning from the rich data sets produced by the key experiments at MPI-SusMat, 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 workhorse 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. The group considers charged point defects as well as 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 (see p. 212).



**Fig. 11:** Configuration coordinate diagram for recombination in CuGaSe<sub>2</sub> at the GaCu antisite defect. The charge-neutral state adopts a DX-like configuration, see inset. The large atomic displacement and the non-parabolic energy profiles enable an efficient carrier capture cycle. Adapted from [33].

In the area of point defects, the group welcomed two short-term visitors (S. Kavanagh from Imperial College London, S. Falletta from École polytechnique federale de Lausanne, EPFL) via the "Coffee with Max-Planck" program to establish new international collaborations, as well as a long-term visiting PhD student (B. Dou, one year). Their work all related to non-radiative recombination. In particular, the defect charge correction scheme was generalized to configuration coordinate diagrams for charge transfer, where ionic and electronic screening effects are imbalanced [78]. Moreover, we investigated the important role of metastable configurations for the recombination pathways [33,79]. Fig. 11 depicts such a non-trivial configuration coordinate diagram for recombination via an DX-like configuration of the GaCu antisite in CuGaSe<sub>2</sub>, an endmember of the Cu(In,Ga)Se<sub>2</sub> ("CIGS") alloy system for photovoltaic applications. The collaboration with the group of R. Hennig (U Florida) on 2D materials continued, too, focusing on the accuracy and limitations of extrapolation schemes [32]. These activities highlight the group's international visibility in the field of defects. A new and challenging direction is to understand off-stoichiometric iron oxides, which are central to iron ore reduction and corrosion. Electron correlation, ionic defects and sublattice disorder, magnetic configurations, and charge localization must be mastered to be able to accurately compute energetic stability and eventually mass transport at the atomistic level (H. Chen).

The methods to simulate surfaces under extreme electric fields, such as encountered in atom probe tomography (APT) or field ion microscopy (FIM), have now been firmly established. The work of S. Bhatt (PhD student) has lifted the theory of field ionization via tunneling in FIM to a new level. By combining DFT simulations for charged surfaces, a new algorithm for wave function tail extrapolation, and the Tersoff-Hamann approximation borrowed from Scanning Tunneling Microscopy (STM) simulations, she was able to predict reliable ionization zones in 3D above model surfaces without further ad-hoc assumptions. The results quantitatively reproduce chemical contrast enhancements for impurities in Ni [15], and qualitatively explain the underlying mechanism by the surface electronic structure, in contrast to previous attempts that exclusively relied on local field variations. The group maintains close bonds to the experimental APT group (B. Gault) and aims at deepening the understanding of APT from a DFT perspective. The prediction of field evaporation characteristics allowed to link field evaporation energy loss spectroscopy (FEELS) contrast [80] to evaporation paths near grain boundaries, see Fig. 12. Also, the influence of the electric field on surface diffusion is being considered (S. Katnagallu). The group's achievements in deepening the theoretical understanding of APT were recognized by awarding the J. H. Block lecture of the APT&M '23 conference to C. Freysoldt, and by his election into the Steering Committee of the International Field Emission Society.

In acknowledgement of his continued service in peer review for the Physical Review Journals, C. Freysoldt was recognized as an 'Outstanding Referee'– a special honour of this journal family, that is given to only a tiny fraction of their active reviewers world-wide (<1 in 5000 per year).

All these method developments would not be possible without the SPHInX package as the code framework, which continues to be worked on. Recent innovations include an efficient algorithm to locate transition states (ricTS) and, as mentioned above, a significantly more versatile version of the sxdefectalign tool for charge corrections that simultaneously supports dielectric anisotropy, multi-center defects, and mixed screening [78]. On-going efforts address support for GPUs (in collaboration with Max Planck Computing and Data Facility) and an extension of the molecular-orbital projectors for DFT+U to capture the coupling of correlated transition metal *d*-orbitals with O ligands in transition metal oxides such as Fe<sub>2</sub>O. In addition, the interfacing of pyiron to the special capabilities of the SPHInX code are gradually progressing. The pyiron/SPHInX interface is a joint effort with members of



**Fig. 12:** Field dependence of field-evaporation barriers from various sites near a  $\Sigma$ 3 symmetric tilt grain boundary in Al. The pathways differ in their roll-over direction, which in terms determines the field sensitivity due to the alignment of the bond-breaking direction with the external field.

the CM department outside the group, and often implies adaptations on both sides to provide a convenient use-experience.

The group is further active in machine-learning from the huge experimental data sets produced in electron microscopy and atom probe tomography. There are unique opportunities coming from data-rich, yet noisy experimental signals that exhibit recurrent, but fuzzily defined patterns. Such data sets demand automated analysis tools that exploit material science domain knowledge. For APT, A. Saxena (PhD 2024) developed a workflow for automatic, largely unsupervised identification of chemical domains (which could represent phases, or defect-related segregation zones) in real space [20]. Depending on the (1D, 2D, 3D ellipsoidal) morphology, additional steps are undertaken to provide a geometry-adapted, guantitative analysis. For instance, for line-like features, skeletonization of their iso-surface traces the core lines (incl. branches & loops), which in turn allow us to map out composition profiles along the running direction and perpendicular to it. This is complemented by a crystallographic plane detection near "poles" of the detector hit map, that relates the crystal orientation to the reconstruction coordinate system. In electron microscopy, we have further explored the use of physics-informed neural networks (PINNs) as a tool for coarse-graining and quantification of transformation kinetics (L. Sreekala, U. Saikia). In recognition of the group's expertise in ML-based data processing for APT and STEM, C. Freysoldt was accepted as an associated member to CRC 270 in 2024.

Yet, turning ML from the proof-of-concept stage to actual tools in the hands of experimentalists remains challenging [44]. First, there is a significant cultural gap between the programming-oriented ML community, and the interactive visual inspection via GUIs predominant in imaging experiments. We aim at addressing this by packaging our algorithms in ready-to-apply workflows, also in collaboration with NFDI (see p. 86) and similar initiatives. Second, building up an adequate "ML literacy" in academic material science in the long run requires people with skills in materials, information or data science, and software development. Each single skill makes young researchers attractive for the non-academic job market; for those who have such skills combined, there is a significant braindrain to industry – on our side as well as for academic

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collaborators. While we support people in their personal careers, extra efforts are needed to encourage a rapid transfer of implicit know-how from the experienced researchers to the newcomers in the available time frame.

# Complex Concentrated Alloys (F. Körmann)

The Complex Concentrated Alloys (CCA) project group of Fritz Körmann focuses on the method development and application to compositionally complex alloys, including the prominent class of high entropy alloys (see p. 226).

A core pillar is developing and advancing machine learning approaches and implementing them into materials acceleration platforms (MAPs) (see p. 232). With this method, we successfully explored the wide range of chemical combinations in high entropy alloys to find compositions that improve the properties of target materials. A collaboration between the MA (see p. 161) and CM departments and the MPI-SusMat fellow group of O. Gutfleisch (see p. 29) led to the discovery of novel Invar alloys that substantially outperformed conventionally designed HEAs [27]. This was achieved by combining advanced machine learning algorithms, *ab initio* calculations, thermodynamic assessments, and eventual casting and measurements of candidate alloys.

Besides these functional materials discoveries, the project group also focused on refractory alloys. These alloys are vital for sustainability because of their exceptional heat resistance and durability. These properties enhance energy efficiency and extend the lifespan of high-temperature industrial components. However, fundamental physical mechanisms relevant to the computational modeling of these alloys, such as the big gualitative difference in anharmonic vibrational contributions among the group V and group VI bcc refractory elements, have not been fully understood. Explicit anharmonic free energies and entropies for Nb, Mo, Ta, and W have been computed [37] to resolve this. It turned out that the difference in the explicit anharmonic values between Nb and Ta in comparison to Mo and W arises not from the high-temperature behavior but rather from the 0 K behavior. Temperature destabilizes the bcc structure of Mo and W, whereas it stabilizes bcc Nb and Ta. In the bcc refractory elements, the anharmonic behavior manifests predominantly in the first nearest and second neighbors. These insights allow effective interaction models to be developed and used for efficiently designing refractory multicomponent alloys.

Melting properties are further critical parameters in the

design of refractory alloys. We calculated high-accura-

cy melting temperatures for V, W, and VW [1]. Based on

these calculations, we could show that thermal vibrations

greatly impact the electronic density of states and thus

considerably affect the electronic contribution to the free

energy. For W, the impact of vibrations on the electron-

ic free energy of solid and liquid is different. This differ-

ence substantially impacts the computed melting point

and triggers a large electronic heat capacity difference

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between solid and liquid. For V, although vibrations likewise affect the electronic free energy, the effect on the melting properties cancels out to a large degree. We observed a similar impact for the binary VW alloy as for W, but slightly weaker. This reveals that electronic free energies are crucial for the future design and application of melting-property calculations for these materials.

In the last period, the project group also focused on the effect of short-range order in complex alloys [42], particularly in the prototypical CrCoNi alloy (see p. 226). The ab initio computations of SRO in CrCoNi are the subject of numerous experimental and theoretical efforts. Different ground state ordering configurations have been suggested, with a recent study proposing an energetically preferable MoPt<sub>a</sub>-like ordering characterized by alternating one layer of Cr atoms and two layers of mixed Co and Ni atoms in the (110) direction [30]. In a detailed investigation of the impact of magnetism on chemical ordering, significant magnetic energies were found in mixed L12/L10 type ordered configurations [81]. These energies are due to strong magnetic exchange interactions and chemical bonding among the constituent elements. The interplay between magnetism and stability depends on the treatment of magnetic fluctuations and may explain opposing experimental and theoretical findings [18].

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Design

**Computational Materials** 





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# Department of Interface Chemistry and Surface Engineering (GO)

M. Rohwerder<sup>1</sup>, J. Neugebauer<sup>2</sup> (provisional department head)

<sup>1</sup>GO, <sup>2</sup>CM

# 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-guestions 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 three research groups and a guest group. 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), Scanning Magnetic Force Microscopy (MFM) 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 guestions that require the scale and interdisciplinarity.

Of crucial importance also in the last three years was again 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 MPI-SusMat, 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 guickly from six in 2014 to two, the Atomistic Modelling (S. Wippermann) and the Corrosion (M. Rohwerder) groups. In 2020, the early career research group "Spectroscopy at Electrochemical Interfaces", headed by M. Rabe, was established in the GO department as joint research group of the MPI-SusMat and the cluster of excellence RE-SOLV (www.solvation.de) located at the Ruhr University Bochum (RUB). The group uses interface spectroscopic methods to study solvation and other dynamic effects on solid surfaces interfaces. By establishing this group important expertise could be regained. However, in August 2022 S. Wippermann followed a call to become professor at the University of Marburg, but could be won to still head a guest group. Furthermore in 2024, another new group was established, the "Surface Science for Future Materials" group headed by P. Jovičević-Klug. Furthermore, in July 2023 M. Stratmann returned to the institute, heading his emeritus group "Electrochemical Surface Science", which is set to support the department's research on that topic (see below).

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. 96).

Research Groups	Scientific Interests	Laboratories
Atomistic Modelling (Guest Group) Spectroscopy at Electrochemical Interfaces Corrosion Surface Science for Future Materials	<ul> <li>Electrochemical Surface Science</li> <li>Catalysis and Corrosion</li> <li>Functional Coatings, Surfaces and Interfaces, Self- Healing</li> <li>Fundamental Research on Surface and Coating Related Process Technology</li> </ul>	<ul> <li>Chemical Analysis/TDA</li> <li>Clean Room</li> <li>Co-deposition (PVD, CVD)</li> <li>µ-Electrochemistry (SFC)</li> <li>Kelvin Probes</li> <li>High-Resolution XPS/ NAP- XPS/SEM/ EDX/ EBSD</li> <li>Optical Spectroscopy</li> <li>Nano IR spectroscopy</li> <li>Scanning Probe Techniques</li> </ul>

Fig. 1: Current research portfolio and expertise.



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



**Fig. 2:** Part of the GO department with M. Stratman during an excursion at the department retreat at Ebernburg Castle in 2022.

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 materials under OER conditions (see e.g. "Corrosion" 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.

Of similar importance are the reactions underlying the hydrogen electrode, i.e. hydrogen evolution reaction (HER) and the hydrogen oxidation reaction (HOR), which are also investigated in depth, during the reporting period especially in regard of hydrogen electrode formation on electrodes that are not immersed in electrolyte. Such electrodes "in the dry" are of great importance for our fundamental investigations on the electrochemical double layer (see "Electrochemical Sciences"), and also for possible applications such as fuel cells.

Several research projects focus on industrial processes such as 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 materials.

# **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 within the institute as well as 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. During the last reporting period we have developed for this 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 of 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, p. 149). For these metals, however, this novel approach has its limitations, due to the limited hydrogen permeability of these metals. Hence, an alternative approach has been developed, based on a fundamental investigation of the hydrogen electrode on forming on these materials for a wide range of electrolyte thickness (i.e. relative humidity) and hydrogen activity adjusted from the gas phase (see "Corrosion" group report, p. 149).

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 p. 157).

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 further developed, (see "Atomistic Modelling" group report, p. 146).

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 MPI-SusMat-RUB early career research group "Spectroscopy at Electrochemical Interfaces" (see below).

# Corrosion

The aim of the department is to obtain fundamental insight into corrosion mechanisms targeting 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. Another key technique are Kelvin probe methods, which have proven to be indispensable for the research of coating delamination, but also for fundamental investigations on atmospheric corrosion.

The investigations by SFC are mainly focused on 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. Examples are the performance of zinc alloy coatings and aluminium alloys. The effect of changes from oxygen free to oxygen containing atmospheres and back on the potential measured by Kelvin probe on the surface are taken as an indicator for the reactivity of the corresponding surface oxide, which was indeed found to correlate well with observed corrosion behaviour, although exceptions were also found. 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. The GO department is involved in corresponding research, such as novel ultra-thin conversion lavers. The main problem, however, is that any development of novel pre-treatments and coating concepts 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, that can be considered a major break-through in our understanding of the rate determining mechanisms of coating delamination and should pro-

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vide a completely new access to computational modelling of the delamination process (see 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. However, this research topic was replaced now by research on direct reduction of iron ores by hydrogen and ammonia, a topic that has now been transferred to the MA department (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 special 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 indepth 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. In the reporting period more industry-like coatings are investigated especially in terms of inhibitor transport and how these inhibitors function at the interface between these coatings and the metal surface (see "Corrosion" 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. Now the main focus was shifted towards surface treatments, such as novel ultra-thin conversion coatings and chromium electro-deposition.

# Surface-bulk interactions

This is a new research topic within the department which focusses at surface and interfacial processes from the metallurgist's point of view. The aim is to investigate how to optimise the microstructure and composition of materials for improved corrosion performance and other properties such as for instance wear and friction. In the reporting period, this research was built up by P. Jovičević-Klug, since 2024 head of SURFACES group (see p.155).

# **Scientific Groups**

# Atomistic Modelling (S. Wippermann)

First principles techniques have revolutionized the way in which theory can help practitioners to explore critical mechanisms that govern reactions and to develop new strategies for materials discovery and design. Yet, the application of these techniques to electrochemical systems is still limited, due to outstanding methodological challenges. One such challenge is the development of robust techniques to control the electrode potential in first principles simulations. A well-known example of how resolving such a challenge via novel concepts can extend the scope of simulations is the development of thermostats. The theory of thermostats is a disruptive algorithmic innovation, that enabled the introduction of temperature control to electronic structure Density Functional Theory (DFT) calculations. The analogue technique for modelling electrochemical systems – potential control – is just emerging.

Within the last reporting period, in close collaboration with the CM department, we introduced a novel technique to control the electrode potential: a "thermopotentiostat". This approach can be used equally well to perform empirical or *ab initio* molecular dynamics simulations. In order to demonstrate the performance of our thermopotentiostat approach, we considered a topic that had gained a lot of attention: recent experiments performed in the Geim group at the 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. Therefore, the presence of solid-water interfaces modifies the dielectric response from a highly polarizeable medium, considered to be the origin of water's unique solvation behaviour, down to a response that is close to the vacuum dielectric constant. Understanding this mechanism and describing it in first principles simulations is crucial, since interfacial water is omnipresent and electrochemical reactions in particular occur within the interfacial water region.

In the present reporting period, we implemented our thermopotentiostat approach into the Vienna *ab initio* simulation package (VASP), one of the most commonly used electronic structure codes. Using the computational electrode proposed by Surendralal *et al.* (Phys. Rev. Lett. 120 (2018) 246801) and our thermopotentiostat implementation, we explored the dielectric properties of nanoconfined water at the *ab initio* molecular dynamics (AIMD) level of theory [1].

Fig. 3 shows electrostatic potential profiles that were obtained for two different applied voltages of 0 V (blue curve) and 4 V (red curve), respectively. The space between the electrodes can be partitioned into three different regions: (i) a hydrophobic gap between the electrode surface and interfacial water, (ii) an interfacial water region, and (iii) a bulk-like water region. For an applied voltage of 4 V, the potential decays linearly and unscreened within the hydrophobic gap regions (orange shaded area). Within the bulk-like region (gray shaded area), the electric field resulting from the externally applied voltage is strongly screened. From the ratio between the slopes of the potentials in the hydrophobic gaps and the bulk region, one directly recovers a dielectric constant of ~ 80, consistent with the experimental value for water.



**Fig. 3:** Schematic representation of the ab initio simulation cell. Grey balls represent electrode surface atoms (Ne), whereas red and white balls denote 0 and H, respectively. Blue and red lines indicate planar-averaged electrostatic potential profiles parallel to the surface normal for applied voltages of 0 V and 4 V, respectively, time-averaged over a trajectory length of 125 ps.

The interfacial water region, in contrast, displays a distinctly different behaviour. At interfaces, water forms stratified structures. This stratification gives rise to potential oscillations within the interfacial water region (green shaded area). In analogy to Friedel oscillations, which originate when screening an electric field with charge carriers of finite size, the wavelength of the potential oscillations reflects the size of the water molecules. The decay length of the oscillations corresponds to the Bjerrum length: the length scale, at which electrostatic interactions are sufficiently screened to become weaker than thermal fluctuations.

In consequence, a considerable part of the electrostatic potential drop applied between the two electrodes occurs within the hydrophobic gap, where the field is essentially unscreened, and inside the interfacial stratified water region. Since both the gap and the interfacial water regions are unable to effectively screen the applied electric field, the total static dielectric constant, as measured by capacitive techniques, is significantly lower for nanoconfined water than that of homogeneous bulk water.

Beyond explaining the qualitative mechanism that is responsible for the strong reduction of the dielectric constant in nanoconfined water, our thermopotentiostat AIMD simulations quantitatively capture the screening behaviour of liquid water at electrified interfaces. From our simulations, we can directly extract the polarization bound charge, that is formed due to the dielectric response of the water to the electrode charge. This quantity is crucial for the construction of future implicit solvent models (see p. 79), that are able to accurately capture the dielectric response of water also in the presence of electrified interfaces.

Figs. 4a and 4b show line profiles of the bound charge densities parallel to the surface normal for applied voltages of 0 V and 4 V, respectively. As expected, inside the bulk-like region, the bound charge densities are zero to within numerical accuracy. Inside the regions of interfacial water, however, the bound charge densities display characteristic oscillations, even at zero applied voltage. The oscillations correspond to the specific structure assumed by water at the interface and, hence, depend on the interfacial chemistry of the specific electrode. This purely *chemical contribution* to the bound charge is to be clearly distinguished from *field-induced contributions* due to the presence of surface charges. For an applied voltage of 4 V, Fig. 4b shows distinct modifications, that coincide with field-induced changes to the internal structure of the solid-water interface, as illustrated by the water number density shown in the bottom of Fig. 4b.

Both the chemical and the field-induced contributions to the dielectric response can be accurately described via the AIMD-derived bound charges. In turn, from the bound charges one can directly obtain the polarization density (Fig. 4c) and the spatially resolved dielectric constant (Fig. 4d). These serve as important benchmarking quantities against which to evaluate the performance of implicit solvent models and machine learning techniques.





**Fig. 4:** *a/b*) Bound charge density profiles of nanoconfined water. *c*) Polarization densities, and *d*) inverse dielectric profile with error bars computed from the bound charges. The dashed line marks the value of  $1/\varepsilon_{r,bulk}$  for liquid water.

Using our new developments, in a joint project with the CM department, we turned to a phenomenon in aqueous metal corrosion that has puzzled generations of scientists: under anodic conditions (electron-deficient), magnesium violently dissolves, accompanied by strong hydrogen evolution (HER). This is a key mechanism, hampering Mg technology. Experimental studies indicated that this process involves the formation of univalent Mg<sup>+</sup> ions in solution. These findings have been largely ignored, because they defy our common chemical understanding and the univalent Mg<sup>+</sup> ions evaded direct experimental observation.

In order to reveal the dissolution mechanism and the nature of the unipositive Mg<sup>+</sup> ions, we performed thermopotentiostat AIMD simulations for interfaces between magnesium and liquid water, taking into account the full complexity of the realistic solid-water interface [2]. The supercell contains two Mg kink atoms, since dissolution is generally understood to proceed via kink-sites. Already during equilibration under open-circuit conditions, a water molecule adsorbed dissociatively at one of the kinksites. Two further H<sub>2</sub>O adsorbed subsequently as intact molecules, forming the beginning of a solvation shell. Under open-circuit conditions, this configuration remained stable on the time scale of our simulations.

In order to drive a dissolution reaction, we subsequently polarized the Mg slab anodically via our thermopotentiostat. Within ~ 5 ps, the solvation shell is completed and the kink-atom is increasingly lifted out of the surface. Although the surface is charged with 2 additional electrons, indicating that the Mg atom is fully ionized, the solvated Mg<sup>2+</sup> ion remains firmly bound to the surface: in conjunction with the hydroxyl group created by the earlier dissociative water adsorption, the solvated ion forms an  $[Mg^{2+}OH]^+$  complex, where the hydroxyl group connects the kink atom to its nearest Mg neighbour. This hydroxyl bridge bond is highly stable and we estimated its binding energy to ~ 2 eV. Such a high binding energy is inconsistent with the experimentally observed high dissolution rates. In order for the dissolution to proceed, the breaking of the hydroxyl bridge bond must be catalyzed by its surrounding environment.

Here, our simulations revealed two possible reaction pathways:

1) A concerted double proton transfer from a neighbouring adsorbed water molecule relocates the hydroxyl group laterally to a neighbouring site. Hence, the  $[Mg^{2+}OH^{-}]^+$ complex is oxidized to  $Mg^{2+}$  and quickly moves into the liquid water region, leaving the hydroxyl group behind on the surface (Fig. 5, upper panel).

2) A single proton transfer within the solvation shell exchanges the positions of the hydroxyl group and one of the water molecules that is part of the solvation shell (Fig. 5, lower panel). Thereby, the  $[Mg^{2+}OH^{-}]^{+}$  complex as a whole becomes solvated and moves into the liquid water region.



**Fig. 5:** Two distinct pathways for Mg dissolution: **(1)** A concerted double proton transfer from a surface adsorbed  $H_2O$  to the hydroxyl bridge releases the  $Mg^{2+}$  ion into solution. **(2)** Alternatively, an intra solvation shell single proton transfer to the hydroxyl bridge equally detaches the  $Mg^{2+}$  ion. The hydroxyl remains attached, resulting in an effectively +1 charged [ $Mg^{2+}OH$ ]<sup>+</sup> complex. For clarity, only the participating water molecules are shown.

The outcome of these two competing processes is fundamentally different. For pathway (1), the hydroxyl remains on the surface. Hence, the surface will be quickly hydroxylated and becomes electrochemically passive. Dissociative water adsorption and therefore any further anomalous hydrogen evolution is no longer possible. Pathway (2) on the other hand, removes the hydroxyl group into solution, leaving the next kink-site exposed to further dissociative water adsorption. It is therefore only pathway (2) that is associated with anomalous HER. Consistent with experimental observations, that only the postulated unipositive  $Mg^+$  ion is associated with the anomalous HER, the  $[Mg^{2+}OH^-]^+$  ion complex created along pathway (2) is effectively charged 1+. We therefore proposed that the elusive unipositive Mg+ ion is, in fact, an  $[Mg^{2+}OH^-]^+$  ion complex.

Via thermopotentiostat AIMD simulations of aqueous magnesium interfaces under potential control, taking into account the full complexity of the realistic metal-water interface, we have discovered a novel and unexpected reaction pathway. The identified dissolution product -[Mg<sup>2+</sup>OH<sup>-</sup>]<sup>+</sup> – naturally explains one of the most studied and debated corrosion mechanisms - the anomalous anodic hydrogen evolution, which has puzzled scientists since it was first reported more than 150 years ago. This pathway bypasses the usual passivation effect of surface films and explains the unusually high anodic corrosion rates and the chemical nature of the postulated Mg<sup>+</sup> ions. The discovery of such an unexpected reaction pathway demonstrates the level and potential that ab initio molecular dynamics simulations have reached, in conjunction with our recent methodological advances in the description of electrochemical interfaces.

These shared activities between the GO and CM departments recently resulted in an invitation from Nature Chemistry Reviews, to review the state-of-the-art in the field of the first principles description of electrified liquid-solid interfaces. At the time of writing, the article is under review [3].

In 2021, the head of the Atomistic Modelling group was offered an associate professorship position at the Philipps-Universität Marburg (UMR). As of August 2022, the group transitioned to UMR and is still active as a guest group at MPI-SusMat [4-7].

# **Corrosion (M. Rohwerder)**

The main scope of this group is to address fundamental questions of corrosion and of surface and coating technology by isolating the crucial problems behind them and designing model experiments and model samples for their systematic investigation. Four exemplary research projects, in collaboration with external partners, that stand guite nicely for the research in the group are: "H2free - Investigation and modelling of hydrogen effusion in electrochemically plated ultra-high-strengthsteels used for landing gear structures" within the Clean-Sky 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; "PredictCorr - Prediction of durability and lifetime of organic coated metals under longterm environmental conditions", financed by the Flamish Research Foundation, and "Coat4Hydrogen", where in the framework of nrw.progress program the focus is on corrosion protective novel materials for bipolar plates.

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), that was described in the last report (Zhong, X. K. et al., Chemelectrochem 8 (2021) 712-718). 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 be shown even for the case that the exit side is not immersed into electrolyte, just as it is of relevance for the situation met during corrosion driven delamination under atmospheric condition.

With this breakthrough it was intended to bring the research of the fundamental mechanisms of delamination to another level. For this, 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 [8,9], 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, chromium 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. The idea of that project was to provide the tools for a long-term prediction of coating performance. At MPI-SusMat, the focus is on unravelling the underlying mechanisms and providing information about the corresponding kinetics. One planned activity was 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 that was developed during the prior reporting period. However, it was found that the rate determining step seems always to be the insertion of the cation at the delamination front, which is the very first step of delamination. These are then migrating from the defect site into the intact interface. This leads to a correlated decrease in potential at the interface, thus enabling the onset of oxygen reduction. For organic coatings on steel and chromium, the oxygen reduction reaction was found to be usually quickly following this decrease of potential.





**Fig. 6:** Sketch of the relative position of the Galvani potentials in the metal and in the phase above it (electrolyte in the defect site, thin water/gel film or organic coating in the delaminating or intact area) and the corresponding electrode potential in case of a) starting situation: corrosion in a defect and intact interface, b) coating delamination (highly concentrated electrolyte in the defect, highly active corrosion), and c) cation insertion/migration along the interface ( dilute electrolyte in the defect, not very active corrosion), for the case of not sufficiently low potential caused by this insertion for resulting in delamination [10].

More precisely, this is always the case when the cations inserting into the interface causes a significant decrease of the potential as to allow onset of a sufficient oxygen reduction. If a too low amount of cations is inserted, the potential is not sufficiently decreased and delamination is not occurring, but just migration. This can be explained by considering the two distinct driving forces for cation movements: potential gradient, and ion concentration gradient. Since the standard chemical potential of the cations in the intact interface is considerably higher than in the electrolyte, a driving force is needed so that cations enter the interface. In fact, for cations there are two: the difference in concentration and in potential. The concentration in the defect filled with electrolyte is significantly higher than that at the interface (initially the concentration is zero at the interface) and the Galvani potential is notably lower at the interface than in the electrolyte in the defect (note that although the electrode potential is higher at the interface, the Galvani potential is lower in the phase above the metal, since the Galvani potential in the metal is the same at the defect and the interface). Hence, both concentration and potential in the defect can serve as driving force for the ingress of cations into the interface. It should be noted that the interfacial properties are most probably changed as a consequence of hydrated ion incorporation at the interface, and therefore, the standard chemical potential of the cations at the interface might not be constant along the interface, changing from more ion containing interface to still intact interface without any migrated ions. This will be especially the case if due to the pulled down electrode potential, caused by the cations moving into the interface, the interface starts to degrade as a consequence of onset of ORR.

Only if sufficient cations enter the interface, the decrease in potential is sufficient for initiating sufficient ORR rates causing then delamination. Then the potential is pulled down towards the value in the defect. This requires a certain minimum concentration of cations in the defect and a certain corrosion activity (negative potential) to provide a high enough difference in electrochemical potential as to drive a sufficiently high amount of cations into the interface for decreasing the potential far enough as to initiate substantial oxygen reduction for resulting in delamination.

This then will lead to galvanic coupling between defect and delaminated interface, leading to nearly the same potentials at the delaminated interface as in the defect. Otherwise, only migration occurs and the potential will usually remain much higher than the one in the defect. The resulting potential profiles along the interface for the different cases are schematically shown in Fig. 6 and [10].

More precisely, if the potential is pulled down low enough to result in sufficient oxygen reduction to result in delamination, then as a consequence of delamination it will be pulled down towards the potential of the defect. However, due to the galvanic coupling there will usually be the according IR drop caused by the ion flow supporting the oxygen reduction rate at the delaminated and delaminating interface.

Interestingly it was found by surface analysis of the delaminated interface after pulling off the organic coating that the concentration of cations at the delaminated interface is proportional to the electrochemical driving force  $\Delta E$ , the factor being the interfacial capacity. This is true also for delaminated regions close to the defect, that are delaminated for relatively long time compared to the regions closer to the front and for which significant charge densities accumulate due to oxygen reduction at the delaminated interface [11]. This means that contrary to the up to now accepted theory, the ion flow necessary to support the interfacial oxygen reduction is not cation migration from the defect to the delaminated interface. but most likely hydroxyl ion migration from the delaminating interface to the defect. The latter are produced in high guantity by the oxygen reduction reaction occurring at the delaminating interface and due to the confined space at the interface very high concentrations of hydroxyl are expected. Hence, the hypothesis that hydroxyl migration towards the defect provide the necessary charge transport for supporting oxygen reduction makes sense.

These results clearly show that the role of cations migrating into the intact interface at the front is that they pull down the potential, just initiating oxygen reduction, followed by delamination. It has been indicated already in the last report and it was confirmed by a considerable number of experiments that the kinetics for this initial process, i.e. the insertion of cations into the intact interface, are rate determining for the whole delamination process and shows a very distinct dependence on the potential drop  $\Delta E$  across the delamination front. This dependence was now found to be very similar for different coating systems and even for different metallic substrates (Fig. 7).



**Fig. 7:** Dependence of delamination/migration rate on a) potential at the beginning of the steep front b) potential difference across the delamination front for PVB and two more resistant, industry-relevant coatings with  $0.5 \text{ M K}_2\text{C}_2\text{O}_4$ ,  $0.5 \text{ M Li}_2\text{C}_2\text{O}_4$ , 1 M KCL and 1 M LiCl as electrolyte in the defect. Two regions with different slopes, shown by solid and dashed lines, are similar in the PVB and the delamination resistant samples [11].

As can be seen from Fig. 7, the slope of the plot of logarithm of delamination/insertion rate against the electrochemical driving force ( $\Delta E$ ) is the same for different coatings, which means that the cation insertion into the intact polymer/iron interface follows the same fundamental mechanism regardless of the coatings chemistry. The chemistry at the interface only shifts the rates to lower or higher values, but the relationship between the rates and the driving force remains unchanged. Even maybe more surprising is that the same slopes were found also for other substrate materials, such as chromium and aluminium. Again, only the absolute values are shifted to lower or higher values, depending on the system. For aluminium, however, the progress of the steep potential front measured by Scanning Kelvin Probe (SKP) is not delamination, but initially only migration of cations, as the insulating oxide on the aluminium does not allow oxygen reduction and thus no cathodic delamination. It was observed, however, that delamination seems to occur with a delay, most likely caused by onset of corrosion at the interface. This is proposed to be caused by anions, such as chloride, which can now that the original opposing potential gradient was lifted by the cation migration can diffuse into the interface. This is object of current research.

It is up to now unclear why the dependence of the logarithm of the delamination rate on  $\Delta E$  seems to be the same for so significantly different systems, for different coatings and different substrates, and why there are two distinct slopes observed for this, one shallower at higher  $\Delta E$  and one steeper for lower  $\Delta E$ . Initially it was assumed

that at lower  $\Delta E$  the interface might not get fully delaminated and that this might have an effect. However, this could not be confirmed as a clear correlation [11]. Another possible explanation is that this might be an artefact of the SKP measurement and the use of  $\Delta E$  in our analysis. In fact, one would envision that the insertion into the intact interface has to occur by numerous atomistic hopping steps. Each individual hopping step of a cation has to overcome an activation barrier that is partially lowered by the electric field caused by the potential drop at the front. That would lead to a Butler-Volmer like dependence of the hopping rate on the potential drop. Although each hopping event will see only a tiny fraction of that potential drop, the high number of hops involved in the macroscopic progress might result in exactly the observed (Tafel like) behaviour. This effect depends on the local electric field along the delamination front region, i.e. the slope of the steep potential transition in the potential profile obtained by SKP. However, a standard Kelvin probe does not have high enough resolution to provide information about the local electric field in such a narrow area. This could be potentially solved by the potential measurement at the front region using Scanning Kelvin Probe Force Microscopy (SKPFM). However, the high resolution of SKPFM is only achievable in case of very thin coatings in the range of a micron or even better below. For thicker coatings the resolution decreases accordingly. Therefore,  $\Delta E$  in the SKP potential profiles was used in this work as a measure for the driving force. In order to enable studies of the cation insertion process, it is hence planned to perform SKPFM studies on the bare substrate without organic coating. It was found that the potential profiles monitored by SKP for the migration of cations from an active corroding defect across the uncovered surface look exactly like the ones during delamination of the organic coating [12,13], i.e. the rate determining step when cation migration proceeds into a yet not migrated surface area is the insertion of the cations at the surface region at the front of the migration zone. Without organic coating SKPFM can provide information about the underlying process with very high resolution, as first results demonstrate [12]. An example is shown below in the section on semiconducting properties of oxide films. In current research it is tried to perform according experiments at different  $\Delta E$ , in order to see how this affects the potential gradients at the migration front. However, that is not easily achieved, due to the space limitations under the SKPFM tip, which makes potentiostatic control of the defect difficult. To solve that problem is object of intense research.

Regardless of this point, as mentioned, the Tafel-like behaviour in Fig. 7 looks the same for the different coatings on different substrates; they are just shifted corresponding to the driving force required for a given rate of the cation insertion, which is higher for resistant coatings. This is of importance not only scientifically, but also practically when there is an interest to model the delamination of different coatings on steel. In fact, once the dependence like the ones shown in Fig. 7 is known for a certain coating system, it would suffice to be able to predict/model the ohmic potential drop along the delaminated interface in order to predict the delamination behaviour [11].

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Furthermore, it was also found by surface analysis of the interface after delamination that the cation migration seems to occur directly along the interface for weaker coatings and rather within a more extended interphase region for stronger ones. This would also mean that for stronger coatings the electrochemical double layer at the interface is more smeared out, implying also lower electrochemical reaction rates, which, however, are not rate determining.

Concluding, break-through achievements were obtained during the reporting period for our understanding of the fundamental process during cathodic delamination, replacing the decades old view that for weak coatings cation migration from the defect to the delamination front is rate determining, resulting a square root of time progress law, and for strong coatings oxygen reduction. Instead in all cases the cation insertion at the front is rate determining. A square root of time progress law is just caused by a steady decrease of  $\Delta E$  due to the ohmic drop across the delaminated interface. Another important insight is that the distribution of nanoscopic pores at the interface plays a role in distinguishing between weak and strong coatings. Interestingly, also the semiconducting properties of the native oxide of the metallic substrate play a role (see below).

#### 2. Intelligent self-healing for corrosion protection

In the prior reporting period, the focus of the research was on the potential of intrinsically conducting polymers (ICPs) for enhancing trigger signal spreading for leading to optimized smart release of active self-healing agents from suitable nano-containers, as well as on in how far ICPs can also increase the transport of these agents towards the corroding defect. For both purposes. macroscopic networks of ICP are necessary to achieve significant improvements. However, such macroscopic networks are lowering the corrosion resistance in case no active agents or too low amounts of active agents are released [14]. This is due to the very fast ICP reduction by fast cation transport in the reduced matrix. 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. Only if the ICP is in contact with sufficient amounts of smart nano-containers loaded by suitable active agents, this negative property can be tuned into a positive one. Due to the cation permselectivity of the reduced ICP, macroscopic networks of ICPs so far did not seem to be suitable for direct storing of active agents and providing their smart release, because counter-anions inside the oxidised conductive form of the ICP, which theoretically could be expected to be released during the reduction, remain in the polymer upon reduction, as cation uptake provides charge neutrality. Now it was found that in fact also smart release is possible directly from ICPs. Non-charged neutral active agents entrapped into the ICP polymer matrix during the deposition process were shown to be safely trapped in the ICP matrix and to be released during its reduction [15]. Indeed, very promising results were obtained by this concept.



**Fig. 8:** Schematic drawings showing three different experimental set-ups. a) Left: a reservoir containing an inhibitor in  $\beta$ -cyclodextrin ( $\beta$ -CD)) is in contact with a zinc substrate coated by a polypyrrole (PPy) layer and a top coating. Delamination proceeds from a small defect in the coating to the reservoir, allowing the diffusion of the inhibitor through the reduced PPy. b) Left: Similar system but without the PPy layer. c) Left: Zinc coated with PPy containing an inhibitor and top coating, with a corroding defect at the left-hand side. Right: Corresponding temporal evolution of the potential in the corroding defect measured by Kelvin probe. After a few hours, passivation occurs in cases (a) and (c) [16].

The smart release is proposed to be caused by the loosening of the ICP polymer chains due the decreased number of hydrogen bonding and subsequent increased mobility, thus providing more permeability through the ICP matrix [16]. An example is shown in Fig. 8 where for the case of the inhibitor in  $\beta$ -cyclodextrin the passivation of a defect site is compared for the case of inhibitor transport from a reservoir with the inhibitor towards the defect through an ICP layer (Fig. 8 a), along the delaminated interface (Fig. 8 b) and from the trapped state within the ICP layer (Fig. 8 c).

Among smart nano-containers of interest, cerium vanadium oxide for smart pH-triggered release of cerium vanadate [17] and pH-sensitive polymer coated mesoporous silica have been found to be guite promising [18]. Mesoporous silica even by itself was found to provide extraordinary strong self-healing potential at the delaminated interface. It was observed that when SiO<sub>2</sub> containing PVB coatings was applied on zinc it was observed to inhibit corrosion-driven organic coating disbondment and even to self-heal the already delaminated interface [19]. The protection mechanism is that meso-porous SiO<sub>2</sub> degrades in the high alkaline pH at the delaminated area and forms a silicate layer that blocks underfilm corrosion and even re-establishes a protective and delamination resistant interface. Such behaviour is of high interest for smart self-healing coatings where a relatively fast delamination progress ensures fast spreading of a trigger signal (e.g.

increase in pH, decrease in potential) for smart release as well as fast transport of the released active agents along the delaminated interface [16]. Once the defect is passivated and maybe even covered by a new polymer coating, the delaminated interface has to be healed, too. This is obviously provided by the silica additions to the coating. It is proposed that as a consequence of the cathodic ORR at the delaminated and delaminating interface the corresponding increase of pH leads to a degradation of the silica in the vicinity of the interface. The silicate released by this degradation forms a protective layer and re-established a protective interface [19].

In a more recent project within the framework of the REDI (RMIT European Doctoral Innovators) PhD training program, co-funded by the European Union and creating new research and enterprise links between Australia and Europe, it is investigated for more resistant, industry-relevant coatings how smart self-healing can be optimised. For this, the focus is on fundamental investigation of self-healing at the buried interface.

### 3. Corrosion

While the main corrosion activity within the department is still on organic coating delamination and intelligent self-healing, in the meanwhile also more classical corrosion topics have re-gained importance. Most notably passive layers and their failure are now of increasing research interest in the department. One main motivation for this is the search for novel materials for bipolar plates and possibly also catalyst supports 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 was the object of research within the project MaxCoat (in cooperation with the hydrogen and fuel cell center ZBT and the Leibniz Institute for Plasma Science and Technology), where MAX phases, which are known to show high conductivity and high chemical stability, are investigated as a possible coating material for bipolar plates. The deposition of Ti<sub>2</sub>AIC MAX-phase coatings turned out to be quite difficult. The structural and chemical characteristics of the Ti<sub>2</sub>AIC MAX phase coatings fabricated using high power impulse magnetron sputtering (HiPIMS), with and without an additional substrate bias were explored. The main difficulty was to achieve the formation of a true MAXphase in the coating. This required a thermal annealing, which due to a non-negligible oxygen partial pressure in the process chamber resulted in the surface layer region of the Ti<sub>a</sub>AIC coating to turn oxidic. However, nevertheless this surface of the annealed coating turned out to be highly corrosion resistant and conductive, as required for bipolar plates. First indications from preliminary longterm cell exposure experiments and contact resistant measurements seem also very promising.

The results obtained in the MAXCoat project clearly show that oxides of valve metals such as Ti and Al potentially can show both very high corrosion resistance as well as high conductivity. While the former is maybe not that surprising, the latter is. In a more recent project,

the Coat4Hvdrogen project in the framework of the "progress.nrw-innovation" program and in cooperation with the Fraunhofer Institute for Material and Beam Technology IWS, it is the aim to performing a larger scale alloy screening in order to investigate how optimized, highly resistant as well as highly conductive materials can be obtained, mainly on basis of valve metals. Of utmost importance here is that in the MAXCoat project it was found that not only composition, but also the phase structure plays an important role. Hence, the research will be based on well characterizable single-phase High Entropy Alloys (HEAs) or more generally Compositionally Complex Alloys (CCAs) valve metal-based bulk samples. The target is also to provide additional data to the up to now quite sparse literature data on this topic, potentially using this for artificial intelligence-based alloy development for corrosion resistant, highly conductive materials, especially for fuel cell and electrolyser applications.

In cooperation with the MA department, guite promising results have already been achieved with deep learning for uncovering compositional and environmental contributions to pitting resistance of more standard passivating alloys [20,21]. Another approach that will be pursued is fundamental in-depth analysis of selected single-phase alloys of interest. For a high-strength Al-Zn-Mg-Cu alloy, for instance, it was possible to build up a direct correlation between the near-atomistic picture of the corrosion oxide film and the solute reactivity in the aqueous corrosion of a high-strength Al-Zn-Mg-Cu alloy. The results also provide direct evidence that the oxide acts as a trap for hydrogen, indicating that Al oxide might act as a kinetic barrier in preventing H embrittlement [22]. As in the last reporting period also tribological degradation phenomena were addressed [23].

# 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 metallic coatings, such as zinc alloy coatings and chromium coatings, as well as surface modification by novel ultra-thin conversion coatings. In general, the composition, structure and the related properties of oxides and conversion layer coatings are of utmost importance for the performance of the organic coating systems deposited onto them. In the past it was thought that the main reaction of interest in this context is the oxygen reduction reaction, i.e. the cathodic reaction branch in the overall corrosion or delamination process. However, for the delamination of organic coatings it was now found that oxygen reduction is not the rate determining step even for very resistant coating systems, but rather the cation insertion at the delamination front. Nevertheless, it is generally observed that coating delamination is clearly correlated to the conductivity of the surface layer, i.e. slower for metals covered by thicker oxide layers or by conversion layers.

This would mean that cation migration on such surfaces is affected by the semiconducting properties of the correlated surface oxide or conversion layer. This is a new



topic of current research, where one of the first steps is to obtain microscopic information about the process [12,13]. Obtaining microscopic information is also highly relevant for a better understanding of the correlation between delamination rate and potential difference across the delamination front, as described in the section on the fundamentals of delamination. One example for such a microscopic study by SKPFM is shown in Fig. 9.



**Fig. 9:** High-resolution 3-D electrode potential-topography mappings obtained during in situ cation migration on the surface of a Cr coated sample featuring strong surface inhomogeneities at different times. The migrating cations are advancing from the upper right corner.

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Another important focus of our research is on the effect of hydrogen on the properties of the oxide in the passive layers of metals, i.e how the work function of different oxide, or rather the electrode potentials established on their surface in different environments, depends on hydrogen activity. This would be important for a better understanding of potential maps obtained by SKP or SKPFM during hydrogen permeation or effusion experiments. While in our research usually ultra-thin PVD-deposited palladium detection layers are used, for which a full calibration of the relation between potential and concentration of hydrogen in the Pd layer is available in the department, nearly all other researchers who use Kelvin probe techniques for monitoring hydrogen in materials measure directly on the oxide covered surface. One recent important observation made in this research is that for such hydrogen mapping it is important to be aware of the fact that the observed potentials are not only due to partial reduction of the surface oxides by the hydrogen effusing from the underlying metal into the oxide layer, but that in parallel there is an equilibrium with an according hydrogen electrode on the oxide surface. On some oxides the correlated protons of the hydrogen electrode seem to possess high mobility, which under certain conditions may result in fast proton migration on the surface, resulting in potential contrasts that are not directly correlated to hydrogen diffusion. This is intense object of current research.

Furthermore, this topic 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 one of the most fascinating results, achieved during the prior reporting period, is that the electrochemical oxygen reduction reaction on the surface of palladium just covered by one to two monolayers of water, is showing similar kinetics as for immersion in acidic bulk electrolyte. However, it is still unclear how electrode potentials measured by the Kelvin probe technique can be interpreted. For instance, in bulk electrolyte the electrode potential of the hydrogen electrode is determined by hydrogen activity and pH in the bulk electrolyte. On an electrode covered by a sub-monolayer or monolayer range water laver especially the pH is unknown. But for in-depth investigation of such "dry" electrodes it is first of all very important to have a reliable reference electrode. Different thicknesses of water layer are adjusted by different humidity. Standard -bulk electrolyte-based-reference electrodes are not stable under these dry conditions. However, there is no surface that is known to be unaffected by changes of relative humidity, due to the correlated adsorption or desorption of water molecules, which due to their significant dipole moment, cause changes of the surface potential. In a systematic work it could be shown now that dry Ag/AgCl electrodes are not only inert in the whole relative humidity range from 0 - 98 % r.h., but also inert against changes of partial pressure of oxygen and hydrogen. In-depth investigations were carried out in order to understand this. Strong indications were obtained that the surface potential of the AqCI on the Aq/AqCI electrode is close to zero and adsorbing water is highly disordered. The resulting potential of the dry electrode can be controlled in a wide range, depending on the formation parameters, but in some cases, this may result in lower inertness. Obtaining such a highly stable reference of the electrodes in the "dry" was an important breakthrough. While the question of how to interpret pH on these electrodes is still quite open, the role of different amounts of adsorbed water molecules on potential and also on kinetics e.g. of oxygen reduction on these electrodes is making good progress. Furthermore, it was found that for the hydrogen electrode on these surfaces the adsorption and desorption kinetics of hydrogen seem to depend similarly on relative humidity, i.e. water layer thickness. For noble metals such as Pt and Ir, the desorption and adsorption reactions are much faster in dry atmosphere than in more humid one. This is another object of current research, as this may be of importance for new design concepts for fuel cells and electrolyses. Currently the hydrogen electrode in the "dry" approach is combined with the concept of emersed electrodes, which provides unique possibilities to tailor electrochemical double layers that would be impossible to achieve in bulk electrochemistry.

Also, of importance are studies on ion mobility on such electrodes in the "dry", as if they are to be used in practice, e.g. in fuel cells, the ion flow between anodic and cathodic electrodes have partly to occur also on these "dry" surfaces.

This research on electrodes in the "dry" is also topic of the emeritus group "Electrochemical Surface Science" of M. Stratmann, with which forces are joined here. Special emphasis of the emeritus group is to investigate the structure of water in the electrochemical double layer and its role on the kinetics of reactions such as oxygen reduction and on ion mobility.

# 6. Measurements of hydrogen distribution and effect on embrittlement

The 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 and within projects, see e.g. [24]. The focus of the current activities on this topic is to develop a new approach is more suitable to resolve hydrogen also in very finely microstructured materials. In this approach, very localised hydrogen uptake is realised, enabling to monitor hydrogen permeation laterally without a smear out effect across the microstructure.

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

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 laboratory, such as the selective oxidation at the surface and at the grain boundaries of various binary and ternary iron-based alloys, this research topic was now concluded with a more fundamental investigation of the grain boundary oxidation of Fe-10 at% Cr, alloy at 200°C, for which a new mechanism is proposed [25], and a study on the selective oxidation of a dedicated quaternary Fe-Mn-Si-Al model alloy, by systematically varying the Al content and dew point of annealing atmosphere. The results indicate that Al has negative as well as positive effects on galvanisability. This work changes the perspective away from a focus solely on the deceleration effect of AI to also consider its acceleration on the surface selective oxidation, providing insights critical for developing strategies against galvanizing problems of AHSSs [26].

As concerns the experiments of direct reduction of iron oxides, the high-temperature laboratory of the GO department has now been fully re-organized to meet the new requirements and was at the end of the reporting period transferred to the MA department. In the meanwhile, it was shown to allow obtaining deep insights into the direct reduction of iron ore by hydrogen [27] and ammonia [28,29].

# Surface Science for Future Materials (P. Jovičević-Klug)

The Surface Science for Future Materials (abbreviation SURFACEs) group is a newly established group, 2024, within the GO department.

In the years 2022-2024, before the group was established, this new research field was introduced by P. Jovičević-Klug, mainly as Alexander-von-Humboldt fellow. The main focus was on the effect of cryogenic treatment on a variety of properties, such as mechanical properties [30-33], wear and galling properties [34], fatigue [33], magnetism [31,35], surface chemistry [35-42] and microstructure [36,38,35,39,33,43]. The research has covered a range of materials including austenitic and martensitic stainless steels [30, 31], high speed steels [30, 32, 33, 36, 35,41,42,44], high alloy ferrous alloys [30,32,33, 35,36,41,42,44], Al-Mg-Si alloys [38,43], bearing steels and cold work tool steels [42]. Furthermore, in research she has also pioneered shallow and deep cryogenic treatments to provide the best guidelines for optimum crvogenic processing [37]. Research has also been carried out into the failure analysis of martensitic stainless steel [31] where it has been investigated how cryogenically processed material can withstand hydrogen embrittlement compared to conventional heat-treated material. The research has already produced some promising results in this direction. In addition to research on ferrous alloys, research has also been carried out on non-ferrous alloys, such as nickel and titanium alloys, which will be the subject of further research in the future.

The group now focuses on understanding complex surface-bulk interactions from different perspectives. The group also aims to understand the mechanisms between surface and underlying bulk interactions from (geo) chemical, surface and physical perspectives (see p. 49).

The group carries out research by combining different techniques and methods such as Atomic Force Microscopy (AFM) with different modes such as Magnetic Force Microscopy (MFM), Electrostatic Force Microscopy (EFM), Conductive Mode (C-AFM), current measurements, Scanning Kelvin Probe Force Microscopy and Kelvin Probe Force Microscopy (SKPFM/KPFM) and Piezo Force Microscopy (PFM). Other techniques used to obtain results include X-ray photoelectron spectroscopy (XPS) with the





**Fig. 10:** a-b represent TEM micrographs of T-EF (tested sample), where locations of SAED patterns are marked with yellow dots from c-e. STEM results for C-EF sample are presented in f-g parts, where main elements such as Cr, Fe, C and V are presented. They were chosen based on the important role, which they have in forming different types of precipitates. In h-i-j the results of APT analysis are presented. Part h represents a 3D model with isosurface of Cr together with Fe, C, VN and Ta. I and j parts represent proxigrams of selected carbide within the sample.

option of in-depth etching and angle resolution, scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (ESBD), transmission electron microscopy (TEM), atom probe tomography (APT), magneto-optical Kerr effect microscopy, Raman microscopy, wear testing, cryogenic processing, corrosion and electrochemical testing. The SURFACEs group is also a regular user of advanced synchrotron and neutron characterisation techniques around the world.

The group aims to understand surface and interfacial processes from the metallurgist's point of view: how to optimise the microstructure and composition of the material for corrosion performance and other properties such as wear, friction, etc.; how to improve the properties of materials (raw or recycled) and their processing in an environmentally friendly and sustainable way that also leads to lower production and maintenance costs; how to support the development and application of (deep) cryogenic processing for science, energy and industry. The group acts as a link between several MPI-SusMat groups through strong synergetic collaboration with the following groups Sustainable Magnets and Recycling, Corrosion, Spectroscopy at Electrochemical Interfaces, Atom Probe Tomography, Sustainable Synthesis of Materials and Microscopy and Diffraction.

The most important results stem from the group's research on cryogenic processing and on ammonia based direct reduction of iron oxide. Cryogenic processing is a type of processing or heat treatment in which the material is exposed to subzero temperatures in order to change its microstructure and thus its final properties, such as corrosion resistance, wear resistance, fatigue resistance, mechanical properties and many other material properties. Cryogenic treatment is divided into three systematically different temperature systems. The first is conventional cold treatment (CCT), where the temperature is reduced to -80°C. CCT has been widely used in the past because it was believed that tempera-tures up to -80°C were sufficient to convert most of the retained austenite in steels to martensite, thereby achieving improved fatigue strength, dimensional stability and wear performance. Shallow cryogenic treatment (SCT) takes place from -80 to -160°C. On the Celsius scale, deep cryogenic treatment (DCT) is below -160°C.

The importance of cryogenic processing application in the energy sector, in particular, for future fusion applications of high Cr ferrous alloys

(EUROFER97) has been outlined in [45]. Importantly, the corrosion and wear resistance properties are improved by a modified microstructure with higher dimensional stability. A novel technique of cryogenic processing (CP) (Fig. 10) was used to produce the desired type of structure that may offer a solution to current challenges in such a high-temperature, high-corrosion and high-radiation environment. The research identifies CP-induced changes not only in microstructure but also in local chemistry and bonding state of key alloying elements. State-of-the-art techniques such as APT and synchrotron-based in situ scanning photoemission spectroscopy have been used to evaluate the correlations and individual phenomena associated with CP. New possibilities for materials processing for future energy applications are opened up by this novel process and its novel microstructural manipulation.

In another example, in collaboration with colleagues from the Slovenian National Building and Civil Engineering Institute, the influence of CP on hydrogen embrittlement susceptibility was investigated [34]. The group also contributed to the work on ammonia-based direct reduction of iron oxides [29], where it was shown that the product of ammonia-based reduction of iron oxides can be modified by nitriding, opening new avenues towards protecting porous sponge iron from reoxidation, potentially easing the challenge in storage and transportation of sponge iron.

# Spectroscopy at Electrochemical Interfaces (M. Rabe)

The early career research group 'Spectroscopy at Electrochemical Interfaces' is a joint research group of MPI-SusMat and the cluster of excellence RESOLV (www.solvation.de). The group studies a diversity of fundamental properties and dynamic processes on solid interfaces using optical interface spectroscopy methods.

In the recent years, the group developed an expertise in the application of photothermal IR nanospectroscopy, namely atomic force microscope-infrared spectroscopy (AFM-IR), for the study of a variety of materials. AFM-IR employs the nanomechanical AFM techniques to measure a materials' thermal expansion upon absorbance of IR light from a tunable laser source and thereby measures vibrational spectroscopy with lateral resolution in the nanometre regime. A specific sample chamber setup has been realized that allows for measuring under high humidities up to 95% to study adsorbed water in materials. For instance, in one project water adsorption in Nafion membranes was studied. Such membranes are essential components in polymer electrolyte membrane (PEM) fuel cells and electrolyzers where they act as solid electrolyte and ensure sufficient water and ion transport. Nafion membranes show a heterogenous nanostructure comprising of amorphous and crystalline domains that can be depicted in AFM by phase imaging. In an AFM-IR study under increasing relative humidity the IR spectra of adsorbed water could be measured. Furthermore, imaging of the water stretching mode absorbance revealed its correlation with the phase contrast. This result constitutes direct spectroscopic evidence that water adsorption in Nafion membranes is enhanced in amorphous domains which act as channels in the PEM setups.

The properties of solid surfaces can be conveniently adjusted and functionalized with polymers, biomolecules and self-assembled monolayers (SAMs). These monolayers are used in multiple applications such as inhibition of corrosion, bioadhesion and fouling, sensors or catalysts. A thorough understanding of the nanostructure of these systems is needed for their knowledge-based design. Measuring monolayers with nano IR spectroscopy requires high sensitivity and is technically challenging. The employed strategy is to use gold coated AFM tips and substrates to enhance the local electromagnetic field at the measuring position. For reaching even single molecule sensitivity a so-called off-resonance method was recently developed (by others). Using this approach, we succeeded in measuring nano IR spectra of single protein molecule on an aptamer-based biosensor (Fig. 11) [46]. The aptasensor is very specific to the Omega variant of the spike protein of SARS-CoV 2 and was developed by our collaborators of the bioelectronics group at the Institute of Biological Information Processing at the Forschungszentrum Jülich. The sensor preparation proceeds typically via SAM formation in a two-step process. First, the aptamers, i.e. short target specific DNA seguences are immobilized on a gold surface, followed by immobilisation of a blocking agent, such as polyethylene glycol (PEG). The structural changes occurring during

this preparation as well as the analyte binding were studied in more detail by AFM-IR, spectroscopic ellipsometry and IR reflectance absorbance spectroscopy [46]. Thereby nanodomains with lateral sizes in the range of a few nanometres could be detected that differ in height. Nano IR spectroscopy gave unique insight into the nature of these nano domains, such as spectroscopic evidence that the domains consist of two different phases one rich in aptamer, the other rich in PEG. Furthermore, the analysis of the nano IR spectra showed that PEG takes place in an amorphous conformation in the PEG rich domains. Ongoing AFM IR studies of PEG SAMs study adsorbed water under elevated humidity, since it is generally assumed that the biofouling resistance of such surface is a consequence of a specific water structure. So far different degree of water adsorption depending on the PEG chain orientation could be detected by AFM-IR.



**Fig. 11:** a) Single molecule nano IR spectra of analyte protein in comparison to nano IR spectrum of underlying receptor layer. IR images recorded at b) 1660 cm<sup>-1</sup> and c) 3350 cm<sup>-1</sup> show single bound analyte proteins with high IR aborbance [46].

An AFM-IR study of SAMs of ionic liquid (IL) molecules on Si as model system for heterogenous catalysts consisting of metallic nanoparticles on supported ionic liquid phases (SILPs) was conducted in collaboration with the Max Planck Institute for Chemical Energy Conversion [47]. The SILPs were prepared on flat Si substrates and were found to be homogenous apart from IL aggregates appearing on the surface. This work showed that for the measurement of monomolecular layers a gold substrate is not necessary and that the field enhancement from a gold coated tip can yield sufficient sensitivity to study monomolecular layers on silicon.

Also, classical vibrational micro spectroscopies with lateral resolutions in the micrometre regime are used to study material properties. For instance, IR microscopy was used to gain high resolution structural insight into the OH distribution within fused quartz crucibles in a joint collaboration project with the Physical Metallurgy group from the department of Materials Science and Engineering of Norwegian University of Science and Technology, Trondheim (Fig. 12) [48]. The crucibles are used in the Czochralski process for Si crystal growth. The OH content in these materials was thought to significantly determine the crucibles' viscosity during the growth process and hence its durability. The heterogeneity of the OH content within the crucibles was found to be strongly influenced by the production conditions. Surprisingly, the





**Fig. 12:** *IR* micro spectroscopy on fused quartz crucibles: A typical *IR* map (overlayed with microscopy image) recorded at the OH stretching peak region represents local OH content (a). The local OH distribution along the crucible walls depends on the manufacturing process and the quality of the raw material (b). Image adapted from [4] under CC by license.

materials viscosity was found to be uncorrelated with the OH content, indicating that so far unknown parameters determine the crucibles local viscosities [48].

In the group exists long-standing experience with the implementation and application of multivariate curve resolution (MCR) techniques to analytical problems in optical spectroscopy. This is currently applied in a project to study solvation shells of nanoparticles (NP) in aqueous solutions. The specific arrangement of solvent molecules close to solutes or solid interfaces are known to influence surface reactivities and hence require a further understanding. However, these solvation shells are a difficult target for optical spectroscopy due to the strong majority of bulk molecules. MCR methods allow to disentangle the spectral contributions of bulk and solvation shell, an approach termed IR or Raman solvation shell spectroscopy.

By these methods solvation shell spectra of commonly applied NP system such as citrate-capped [49] and pure (prepared by pulsed laser ablation) Au NPs or  $TiO_2$  NPs are studied. Significant differences in the hydrogen-bond strength of the solvation shell water with respect to the bulk were found and the analysis and interpretation of these results is ongoing work.

Electro responsive 'smart' interfaces are another topic

where research has been conducted. In particular, the

electrochemically triggered reduction of germanium

surfaces from OH to H termination was employed as a

hydrophilic/hydrophobic reversibly switchable, 'smart'

interface [50]. By means of electrochemical in situ atten-

uated total reflection (ATR) IR spectroscopy, it was shown

that the hydrophobicity switch can reversibly trigger ad-/

desorption as well as orientation change of amphipathic

model peptides. The observed process (ad-/desorption

or orientation change) depends on the adsorbates charge

distribution, which indicates that a sensitive balance be-

tween hydrophobic and electrostatic interactions gov-

erns the surface attachment. Current work on this project

studies the reversible adsorption as well as structural changes of biological proteins upon interaction with the

switchable Ge surface. Such work generates valuable in-

tions and biofouling. Further research activities focus on the study

sight into the control of protein surface interac-

of electrochemical systems such as electrocatalysts or electroactive systems by means of ex situ and in situ/operando optical spectroscopies and X-ray absorption spectroscopy [51]. In in-house collaborations with the NG group, electrochemical phase transformations and hydrogen evolution catalysts were studied with these methods [52,53]. Within the large-scale network "PrometH2eus" (see p. 94) nickel-based anode materials for alkaline water electrolysers are studied with operando vibrational spectroscopies and other techniques. The anodic oxygen evolution reaction (OER) is generally considered the energetic bottleneck in the production of green hydrogen by alkaline water electrolysis, which can be improved by further development

of suitable electrocatalysts and anode materials. Within this project, electrochemical *in situ* surface enhanced Raman spectroscopy (SERS) on nickel meshes as used in industrial electrolysers has been realized and studies of the effect of iron incorporation in NiOOH catalysts have been performed [54]. The boosting effect of trace amounts of iron in these systems is well known, but little understood. The incorporation by means of a simple coating in solutions of different iron salts was found to have various effects on the OER activity as well as stability of the materials. The *in situ* spectroscopic measurements could verify the active catalyst phases. In the systems studied in this work, catalyst degradation was however a serious problem that needs to be overcome for application.

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# Department of Microstructure Physics and Alloy Design (MA)

D. Raabe

# Introduction

**Research Field and Mission:** The department of Microstructure Physics and Alloy Design conducts research on the relationships between sustainable synthesis, processing, microstructure, and properties of complex nanostructured materials, mainly metals [1–3].

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For revealing the underlying scientific laws behind these relations we conduct model experiments under well-defined boundary conditions and compare them with predictions from physics- and machine learning-based simulations [4-6]. We study microstructures and processes from the atomic level up to the mesoscopic scale with the aim to relate these findings to material properties, using a suite of advanced microscopy and spectroscopy tools in tandem with theory [7–10]. This is often done in cooperation with the other departments. For example, correlative atom probe tomography, electron microscopy and spectroscopy are conducted with the department of G. Dehm and the group of C. Scheu (see p. 17), theory, artificial intelligence and simulations are conducted in cooperation with the department of J. Neugebauer (see p. 125), and hydrogen-based sustainable metallurgy process development in conjunction with in-operando probing are done together with the team of M. Rohwerder (see p. 143).

These insights enable us to yield understanding about basic process-structure-property relations [11–17], leverage novel sustainable metallurgical synthesis processes [1,18–21], and derive next generation probing, reactor, theory and machine learning methods for the development of advanced (metallic) materials and processes [5,22–25]. This report gives an overview of the department's structure and activities, highlighting novel methodologies and scientific highlights from the past 6 years.

**Our Grand Goal: A Basic Science Perspective on Sustainable Metallurgy:** Metal production stands for 40 % of industrial greenhouse gas emissions, 10 % of global energy consumption, and the extraction of 3.2 billion tonnes of minerals annually. Thus, enhancing the sustainability of the global metallurgical sector is both, urgent and imperative (Fig. 1).

The role of alloys in a circular economy, from steels to aluminium and magnets, is essential and requires intense research on the effects of the massive increase in the use of scrap in contaminant-tolerant high-performance alloys. However, research on metallurgical opportunities and limits in secondary synthesis alone is insufficient, as the global market demand for metals exceeds scrap availability by approximately two-thirds. Hence, sustainable primary synthesis methods with less pollutant production, energy consumption, and  $CO_2$  emissions must be explored as well. A third direction in sustainable metallurgical synthesis (also referred to as tertiary synthesis) lies in using already dumped and very costly waste material as feedstock for metal production (Fig. 2).



**Fig. 1:** Entering into the age of sustainability and circularity, where materials occupy key roles with very high leverage in terms of  $CO_2$  emissions, embodied energy, value produced, and strategic relevance [2].

The changes required to reach the sketched sustainability targets (be it in primary, secondary, or tertiary synthesis) are so disruptive, must embrace practically all elements in the periodic table, and also need to consider social, ethical and business aspects, that this means nothing less than the re-invention of an entire industry, which is today the backbone of human society.



**Fig. 2:** Example of the many types of possible feedstocks and reductants in sustainable steel production [2].

While society is meanwhile in principle aware of the necessity to mitigate the environmental impact of the metallurgical sector, the basic materials science needed to reach these targets by leveraging innovative synthesis and process approaches is still in its infancy. This kind of basic research establishes a novel high-risk field that





**Fig. 3**: Example of tertiary production, in which sustainable iron is extracted from red mud, a Bauxite residue, by using H-based plasma reduction [21].

includes multiple disciplines and methods. This means the field of sustainable metallurgy does not constitute a homogeneous or well-established domain, but it emerges from the process- and property-specific questions, which requires input from thermodynamics, kinetics, microstructure, in-operando techniques, mechanics, multi-component chemistry, physics of complex systems, and advanced primary (minerals) [2], secondary (scrap) [1], and tertiary (remined) [21] process and manufacturing methods (Fig. 3).

Equipped with such a grand goal and motivation, the department devotes all its efforts to understand, invent, and enable advanced materials and processes for a sustainable metallurgy and materials sector [1,2]. The following paragraphs illuminate our approaches to pursue these goals.

# Department structure and research groups

The department's work rests on competence centers in the form of research groups, which also act as organisational units. Some of the groups are long-term initiatives and pursue method development, paired with the investigation of specific materials-related fundamental questions, of high scientific and strategic relevance for the institute's mission. Other groups are mid-term oriented, to give new research topics room for fast growth and exploration. While the former ones are core funded by the institute's basic budget, the latter ones are usually non-permanent and extramurally funded. This flexible structure allows us to rapidly pick up new ideas and provide opportunities to young scientists to realize own scientific ideas and develop leadership skills.

Many of these non-permanent groups are not associated with a single department but they are placed between several departments and sometimes between the institute and extramural partner institutions (such as partner universities and the Fraunhofer Society, see p. 31-39). Funding for these initiatives comes from the Max Planck-Fraunhofer collaboration fund, the European Research Council, German Research Foundation, Federal Ministry of Education and Research, and VW Foundation. The main task of these groups is to tackle emerging high-risk topics that require intense cross-disciplinary research, tapping competences from several departments and extramural research groups.

The non-permanent groups are not only hubs to tackle new scientific challenges but they also act as career instruments to prepare postdoctoral researchers for their next steps. This approach of giving young talents both, responsibility paired with scientific freedom, has turned out to be a very successful career propellant, with >20 recruitments of such group leaders on professorships in the last 6 years alone. The interdepartmental und partner groups showcase their work in a separate section of this report (see p. 204).

# Long-term research groups

The long-term groups in the department work on Mechanism-based Alloy Design (D. Ponge), Atom Probe Tomography (B. Gault), Computational Sustainable Metallurgy (J. Mianroodi, until 2023), Microscopy and Diffraction (S. Zaefferer), Microstructure and Interfaces of Batteries (Y. Joshi, new group as of 2024), andTheory and Simulation (F. Roters).

### Atom Probe Tomography (B. Gault)

Atom probe tomography (APT) provides three-dimensional elemental mapping with subnanometre resolution. Insights from APT help understand phase formation and transformations, segregation at interfaces, and partitioning between phases. The group focuses on both applying this burgeoning microscopy and microanalysis technique to a wide range of advanced materials, and to develop both novel experimental setups and data processing techniques.

The group's research has an emphasis on correlating APT with other experimental and computational techniques, with strong collaborations with the research groups Mechanism-based Alloy Design, Microstructure and Interfaces of Battery Materials, Defect Chemistry and Spectroscopy, Electrochemistry and Corrosion, Computational Phase Studies, and Nanoanalytics and Interfaces.

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, leveraging also capabilities for field-ion microscopy (FIM). This was followed in February 2017, by a LEAP 5000 XR, i.e. a reflectron fitted for increased mass resolution. The LEAP 3000 instrument was replaced in 2019 by another LEAP 5000 XR. These instruments offer a wide field-of-view, high detection efficiency, and new generation of UV lasers. These instruments are complemented by three Dual Beam scanning-electron microscope / focused ion gallium beam (SEM-FIB, Helios 600, 600i, 5) and a Helios PFIB with a Xe-plasma ion source. The group operates the world-unique Laplace Project [26], a suite of instruments including a LEAP 5000 XS and a LEAP 5000 XR, a N2-glovebox, two SEM/FIBs and a custom designed laser-equipped reaction cell for APT specimens [27]. These are interconnected with ultra-high-vacuum cryo-enabled suitcases allowing for controlled transport of APT specimens across devices.

Recent highlights from the group are enabled by the development of cryogenic methods for specimen preparation [28,29]. This was the starting point for experiments in battery research [28,29], with analyses of cathode and anode materials, frozen liquid electrolytes [29], liquid solid interfaces [30] including reactive interfaces 'frozen in time' [31] to investigate metastable interfacial states. along with studies of hydrogen in metal [7,17] (Fig. 4), in part associated to stress-corrosion cracking [32]. In addition, the group has made strides into the design of catalysts, with an emphasis on reactions for hydrogen generation [33,34] and magnetic materials, as they are key materials for clean energy generation. The group is also developing novel experimental approaches around FIM, coupled with theory [35,36]. Finally, the group has been at the forefront of the use of machine learning approaches for APT data processing, for data segmentation [37] and retrieving short-range order information [38]



**Fig. 4:** Example of the analysis of liquid solid interfaces by use of atom probe tomography. (A–C) SEM images of the early-stage of aqueous corrosion of Mg microalloyed with Ca, showing the evolution of the corrosion layers over time. (D) Corresponding APT analysis, in which an iso-concentration surface of 15 at. % O and 1.5 at. % Ca helps visualize the corroded layer. (E) 2D composition map from ROI#1 highlights the presence of different corrosion products, while the profile obtained in ROI#2 allows for quantifying the different hydr/-oxide layers. ROI: Region of Interest, selected from data set.

## Computational Sustainable Metallurgy (J. Mianroodi, until 2023)

The group tackled emerging scientific and technological challenges in the field of sustainable material engineering, metallurgy, steel production, energy storage. battery technology, and recycling with a focus on the use of machine learning and physics-based mean field methods such as the phase field simulation approach [6,25]. 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 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. The group thus focussed on developing and using computational methods to solve various challenges related to materials and processes with important environmental impact, placing attention on problems where the interplay of chemistry, phase transformation, microstructure, mechanics, and damage are important.

One example was the simulation of hydrogen-based direct reduction of iron ore as an alternative method of steel production with considerably lower emission compared to conventional fossil carbon-based reduction for instance in blast furnaces. Modelling the reduction process by coupled chemo-mechanical phase-field methods including microstructure and defect evolution was

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an essential research topic in this group. Corrosion and damage evolution during the life cycle of metals is one of the most important underlying reasons 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 were hence also in the focus of projects in this group [39].

## Mechanism-based Alloy Design (D. Ponge)

The main focus in this group is to identify relevant mechanisms to create novel microstructures down from the nanoscale with improved combinations of mechanical or functional properties. In order to develop sustainable materials, the research concentrates on four categories: (1) Alloys supporting light weighting in transportation like high strength steels and Al alloys; (2) New high strength materials with increased resistance against hydrogen embrittlement; (3) Increased usage of available scrap to enhance recycling or upcycling rates; (4) New austenitic steels for cryogenic applications (e.g. for storage or transportation of liquid or cryo-compressed hydrogen) with substitution of expensive Ni by less expensive Mn. In all these four categories the identification of failure mechanisms during deformation, especially in harsh environments like hydrogen containing environments or at cryogenic temperatures is essential. Projects in the group make intense use of the processing, mechanical testing, and microstructure characterization facilities at MPI-SusMat 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 such complex alloys. In category (2) we start with identifying the failure mechanisms during hydrogen embrittlement. Typical for different types of high strength steels is a premature brittle failure along grain boundaries or interphase boundaries. Countermeasures like increasing the cohesion of such weak interfaces by boron segregation are successful in decreasing the sensitivity for hydrogen embrittlement. In martensitic steels we observe boron segregation only at prior austenite grain boundaries. In order to protect also other boundaries like block-, packet-, and lath-boundaries, we are developing a treatment to redistribute boron to all boundaries. In high strength transformation induced plasticity (TRIP) steels, the austenite to martensite transformation during plastic deformation is desired due to its enhancement of the strain hardening rate, preventing strain localization and early necking. But tensile testing of hydrogen pre-charged samples reveals a high ductility loss. This is linked to the TRIP effect: The fresh martensite inherits the hydrogen from the austenite. This favours interface cracking [40,41]. As a countermeasure we showed that for medium Mn steels metastable austenite and austenite with higher mechanical stability can be combined in the microstructure. The austenite with higher stability blunts cracks and leads to an increased resistance against hydrogen embrittlement [40,41]. Fig. 5 illustrates examples for our research in category (3) to support the increased usage of contaminated scrap in re-



Fig. 5: Examples of the research on recycled Al-alloys from contaminated Al scrap (a) Design of Fe-contaminated scrapbased cast AI-Si alloys: Thermodynamic and kinetic metrics were employed to identify the compositions that tolerate higher Fe concentrations (blue in the colour-coded composition map). These compositions promote the formation of the preferred "Chinese-script" phase and suppress the undesired platelet phases, in addition to the refinement of the platelet phases. (b) Effect of Nd on wrought Al-Zn alloys: the presence of Nd, often found in steering systems, electrical motors, and printed circuit boards (PCBs), contaminates AI alloys if scrap was improperly sorted. Here, the APT results confirm the predictions of thermodynamic calculations with FactSage® about the occurrence and composition of NdCu AI. This hard intermetallic phase is problematic because, due to its high melting point, a homogenization treatment is not able to dissolve it.

cycled Al-alloys. The study on cast Al-Si alloys employs thermodynamic techniques to understand Fe impurity tolerance and Mn doping, offering guidelines for sustainable alloy design. Furthermore, it investigates the potential for upcycling impurity-contaminated alloys through thermomechanical processing. The research on wrought high strength 7xxx series Al alloys explores the impact of Fe/Si impurities on microstructure, mechanical properties, age hardening response, and corrosion resistance; in addition to the influence of Mn and Nd doping.

### Microscopy and Diffraction (S. Zaefferer)

This group works on two interconnected tasks: first, it aims at understanding microstructure formation mechanisms and the relation between microstructures and properties of materials by investigations on the microscopic level. Second, to this aim the group develops or advances novel microscopy and diffraction techniques mainly for scanning electron microscopy (SEM). Additionally, the group provides several high-end SEMs, together with latest analysis techniques and extended expertise to everyone in the institute.

The currently best SEM with thermal field emission gun (FEG) is equipped with an electron backscatter diffraction (EBSD) camera with direct electron detection (DED), an energy dispersive x-ray (EDX) detector with large silicon nitride entrance window, a cathodoluminescence (CL) spectrometer with sensitivity from UV to IR wavelengths, and dedicated equipment for controlled electron channelling contrast imaging (cECCI). This particular SEM allows significant advancements, for example in the area of additive manufacturing (AM) where we studied the dislocation evolution in Ti-42 Nb allovs produced by laser powder bed fusion during low cycle fatigue using cECCI [42]. In another project, the simultaneous measurement of high resolution EBSD and EDS, allowed a much-improved separation of austenite, ferrite, bainite, and martensite in DP steels. The DED EBSD camera, furthermore, allows the accurate distinction of the 3 c-axes variants of y-TiAl due to the clear observation of superlattice reflections in TiAl intermetallics. The recently introduced spherical indexing of EBSD patterns has enabled, for example, the distinction of the tetragonal and orthorhombic polytypes of FeSi<sub>2</sub> in very thin sputtered films for photovoltaic applications. Here it is also planned to use the CL system to investigate the relation between microstructure and photovoltaic properties.

One particularly strong aspect of our equipment is the possibility to perform correlative observations of the same sample position with different techniques. A recent important research achievement made by correlation of ECCI, EBSD, and atom probe tomography, together with theoretical calculations by molecular statics is the proposal of a new mechanism for the formation of the sharp Goss texture in Fe 3 % Si, soft magnetic electrical steel [43]. The mechanism called "dislocation-aided particle dissolution" claims that dislocations that are present only in Goss-oriented grains help dissolving the grain growth-inhibiting particles during box annealing of the material and thus enable abnormal growth of these grains. Fig. 6 shows an



**Fig. 6:** Correlative microscopy combining light microscopy, EBSD, ECCI, TEM, and APT to show that dislocations present in abnormally grown Goss-oriented grains absorb the inhibitor elements (AIN) and thus contribute to the dissolution of the growth-inhibiting particles on the grain boundaries. The molecular statics (MS) calculation of segregation to dislocations and to grain boundaries shows that the equilibrium concentration of AI is ten times higher on a dislocation than it is on a grain boundary.

overview on the correlative microscopy approach used here.

A second highly specialized high-resolution SEM is also equipped for cECCI and, additionally, with a dedicated EBSD camera for residual stress measurements using cross-correlation (CC) analysis of EBSD patterns. CC EBSD has been used, for example, for the measurement of residual stresses in AM produced high entropy alloy samples [44].

A final instrument to be mentioned is a Zeiss XB 1450 dual beam FIB-SEM. This system is dedicated to 3D EBSD measurements by serial sectioning using either a FIB, for small volumes, or robot-controlled fully automated mechano-chemical polishing for very large volumes that allow the scale bridging from micrometre-sized measured voxels to millimetre-sized sample volumes. This latter technique has been named "EBSD-based large volume 3D microstructure measurement, ELAVO-3D" [45]. It has been applied to investigate the 3D-microstructure of 3D printed Ti-42 Nb and 316 stainless steel samples [46].

# Theory and Simulation (F. Roters)

The focus of the group is the development of continuum scale constitutive models for crystalline materials. While crystal plasticity models are still at the core of these activities they have been extended in the direction of multi-field simulations in the recent years. Including phase transformation, development of temperature, damage and fracture into the simulations is key in understanding and predicting the properties of nowadays high-performance materials.

High-strength steels usually comprise a complex multiphase microstructure. Here martensite and bainite are among the most complex phases due to their hierarchical structure. A tool has been developed to create representative volume elements of these phases (Fig. 7, [47]) which were used to study the behaviour of different bainitic steels [48].

To facilitate the application of complex multi-field simulations, the group is developing the Düsseldorf Advanced Material Simulation Kit (DAMASK, <u>damask-multiphysics</u>. <u>org</u>). Version 3 of which has been recently released (see p. 78). DAMASK ensures easy extendibility by its modular structure and the pre- and post-processing tools enable combination with other simulation programs.

One example for the latter is the combination of DAMASK with a cellular automaton program for the simulation of dynamic recrystallisation during hot rolling [49].

Many of the simulations of iron ore reduction and degradation of Li-ion batteries are built on top DAMASK [50], making use of its easy extendibility.

The current work of the group focuses on two topics: 1. Making the constitutive models of DAMASK directly dependant on chemistry [51]. This is important with respect to two current developments, namely the building up of a hydrogen infrastructure and making metals more sustainable by an increased use of scrap. A predictive modelling of the connected changes of the material properties is key for the realization of these scenarios. 2. Improved damage models. Predicting damage and fracture of materials is essential for making them more sustainable as one of the best ways to achieve this, is an increased lifetime of components in use.



**Fig. 7:** Creating a martensite RVE. (a) Raw experimental microstructure (includes retained austenite). (b) Prior austenitic microstructure. Black colour means no indexing was possible. (c) Synthetic austenitic microstructure in 3D. (d) Martensitic microstructure. Black lines in (c,d) represents austenite grain boundaries.

# Microstructure and Interfaces of Battery Materials (Y. Joshi)

This new group explores the fundamental microstructural aspects of batteries, considering lithium-sulfur, sodium ion, iron-air batteries, as well as solid-state Li/Na ion batteries, in terms of capacity and longevity. Focus is placed on critical features namely the microstructural and interfacial design of the electrode and solid-electrolytes (for the case of solid-state batteries). Projects target questions related to ionic transport in the electrode and interfacial reactions at the anode, or electro-chemo-mechanical failure or lithium nucleation in anode-free batteries. The group was established very recently and details are given in a separate section (see p. 48).

# **Non-Permanent Research Groups**

Most of the recently established non-permanent and interdepartmental groups are presented in separate sections. The group on sustainable metallurgy, funded by an ERC Advanced Grant, has strong attachment to the department and is therefore presented in the following.

## Sustainable Synthesis of Materials (Y. Ma, R. Souza Filho)

This group is funded by a recently granted ERC Advanced Grant Project about the basic science behind sustainable metallurgical synthesis and processing [1,2,21]. Engineering materials, especially metallic alloys, have driven technological progress for millennia. Metallic materials have enabled significant advancements, from the Bronze Age onward, due to properties such as strength, hardness, workability, damage tolerance, joinability, ductility, toughness, corrosion resistance, thermal and electric conductivity, and magnetism. The increasing demand for structural and functional metallic alloys in sectors like energy, construction, safety, and transportation is projected to grow up to 200 % by 2050. However, the extraction and manufacturing of these materials, particularly steel, aluminium, nickel, and titanium, are energy-intensive and contribute significantly to global warming greenhouse and pollution. Therefore, disruptively improving the sustainability of metals through research in areas like reducing CO<sub>2</sub>-intense primary production [18,19,21,52], low-energy metallurgical synthesis [53], recycling [1-3,20], scrap-compatible alloy design [1], improved alloy longevity [23,54-57], and energy conversion via metal powder combustion [58,59] has today become of the most essential goals in this field. The team develops and operates several custom-made laboratory-scale reactors in which corresponding experiments can be conducted, under well-controlled reactive atmosphere, temperature and mass-balance control as well as in-operando spectroscopy monitoring. Many of these experiments are conducted in cooperation with the group of M. Rohwerder at the GO department (see p. 143). Near atomic scale experiments are done using either in-operando electron microscopes with dedicated sample holders or in collaboration with the Ernst-Ruska Laboratory at the research Center in Jülich. Quasi in situ reduction experiments are also done in the in-house atom probe tomography laboratory in conjunction with the custom-designed reaction chamber and cryogenic-UHV sample exchange unit. Details of the group's activities are presented in a separate section on p. 65.

# Integrated Computational Materials Engineering (M. Diehl)

The Integrated Computational Materials Engineering (ICME) group was established in 2019 and is headed by M. Diehl, who is now assistant professor at KU Leuven, Belgium. The mission of the group is the design and implementation of computational tools for materials science and engineering. To enable wide-spread use of the resulting software solutions, they are released under open source licenses. A strong focus of the group's work is the development of DAMASK together with the Theory and Simulation group of F. Roters. Highlights of this collaboration in recent years were the release of DAMASK 3.0 and the dissertation of 5 PhD students (1

at TU Delft, 4 at RWTH Aachen University) [60,49,61,62]. For an overview of the DAMASK improvements we refer to page 78. A new topic is the design of software for analysis of atom probe tomography (APT) experiments in collaboration with B. Gault. In the DFG-funded project, a unified framework for conventional and machine learning-based data analysis will be developed and released as open source software.

The collaboration between KU Leuven and MPI-SusMat lead also to two successful applications to Research and Innovation Actions (RIA) of the European Commission: In HyWay (started Jan. 2024, p.103), the group collaborates with F. Roters and J. Duarte and 17 other partners to develop computational tools to study hydrogen embrittlement in steels and in FULL-MAP (anticipated start Jan. 2025) a consortium of 32 partners, including also Y. Joshi and C. Liu from MPI-SusMat will develop an integrated platform for the design of novel materials for battery applications.

All the other non-permanent groups are presented within separate sections in this report, as they have either been installed only recently and / or are operated as interdepartmental groups between the established departments.

# **Recent Scientific Breakthroughs**

With these core competences described above, we tackled a few 'Grand Challenges', involving also colleagues from the other departments and from extramural partner groups. Further details about some of these projects are given in the section "Interdepartmental Research Activities - Selected Highlights". Some of the main scientific breakthroughs of the last 6 years are presented in the following

Part I: Sustainable metallurgical primary, secondary and tertiary synthesis.

Can we produce green steel by using ammonia as a reductant carrier? We have recently shown how to make sustainable steel by reducing solid iron oxides with hydrogen released from ammonia [63]. Ammonia is an annually 180 million ton traded chemical energy carrier, with established transcontinental logistics and low liquefaction costs. It can be synthesized with green hydrogen and release hydrogen again through the reduction reaction. This advantage connects it with green iron making, for replacing fossil reductants. We found that ammonia-based reduction of iron oxide proceeds through an autocatalytic reaction, is kinetically as effective as hydrogen-based direct reduction, yields the same metallization, and can be industrially realized with existing technologies. The produced iron/iron nitride mixture can be subsequently molten in an electric arc furnace (or co-charged into a converter) to adjust the chemical composition to the target steel grades.

What is the role of microstructure in hydrogen-based direct reduction? Although this reaction has been studied for decades, its kinetics is not well understood, particularly during the wüstite-to-iron reduction step which is much slower than the hematite-to-magnetite reduction step. Some rate-limiting factors of this reaction are determined by the microstructure and local chemistry of the ores [6,18,19,64]. We conducted a multi-scale structure and composition analysis of iron reduced from hematite with pure  $H_{2^{\prime}}$  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 such studies, we aim to open the perspective in the field of carbon-neutral iron production from macroscopic processing towards better understanding of the under-lying microscopic transport and reduction mechanisms and kinetics.



Fig. 8: Some hierarchy and size scales in the analysis of hydrogen based direct reduction of hematite iron oxides [19]. Following the arrow: hematite ore, sintered pellets, cut pellet, some features of the inner microstructure of the pellets viewed at different scales and reduction stages [52], images of phases and atom probe image of the wüstite-iron interface [65].

What is the influence of porosity in hydrogen-based direct reduction for green steel making? When solid-state redox-driven phase transformations are associated with mass loss, such as in the case of hydrogen-based solid state direct reduction of metal oxides, vacancies are produced that coalesce into clusters and develop further into pores [27,52,64,65]. These pores can influence the kinetics of certain redox and phase transformation steps. We

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investigated in a series of experiments the structural and chemical mechanisms in and at pores in such partially and fully reduced oxides using combined experimental-theoretical methods, mostly on iron oxide reduced by hydrogen as a model system. The redox product (water) accumulates inside the pores and shifts the local equilibrium at the already reduced material back toward re-oxidation into cubic Fe<sub>1-x</sub>O (where x refers to Fe deficiency). This effect helps to understand the sluggish reduction of cubic Fe<sub>1-x</sub>O by hydrogen, a key process for future sustainable steelmaking.

#### Can iron be used as combustion feedstock for the energy

system? Iron can in future also play an important role as feedstock for combustion in conventional power plants [58.59]. To transition from fossil-fuel to sustainable carbon-free energy carriers, a safe, stable and high-density energy storage technology is required, which gualifies iron powders as a promising material in this regard. Yet, little is known about the in-process morphological and microstructural evolution of such powders, which are critical features for the circularity of the concept, especially the subsequent reduction of the combusted oxide powders back to iron. We therefore investigated two types of iron powder combustion pathways, one in air and one with the assistance of a propane pilot flame. Both processes resulted in spherical hollow particles composed of a complex microstructure of wüstite, magnetite and/ or hematite. Partial evaporation is indicated by the observation of nanoparticles on the micro-sized combustion products. The associated gas production inside the liquid droplet could be the origin of the internal porosity and micro-explosion events. Cracking at the end of combustion results in mostly open porosity, which is favourable for the subsequent reduction process. With this study, we aim to open the perspective of iron metal fuel from macroscopic combustion analysis towards a better understanding of the underlying microscopic thermodynamic, kinetic, microstructural, and thermomechanical mechanisms.

How does water get trapped in direct reduced iron? Gassolid reactions are important for many redox processes that underpin the energy and sustainability transition. This applies particularly to the specific case of hydrogen-based iron oxide reduction. Our understanding of gas-solid reactions has so far been limited by the availability of stateof-the-art techniques, which can delve into the structure and chemistry of the reacted solids, and we also missed so far an important reaction partner that defines the thermodynamics and kinetics of gas phase reactions: the gas molecules. In a set of experiments, cryogenic-atom probe tomography has been used to study the guasi in situ evolution of iron oxide in the solid and gas phases of the direct reduction of iron oxide by deuterium gas at 700 °C [27,52,64,65]. We observed several atomic-scale characteristics, including, D2 accumulation at the reaction interface; formation of a core (wüstite)-shell (iron) structure; inbound diffusion of D through the iron layer and partitioning of D among phases and defects; outbound diffusion of oxygen through the wüstite and/or through the iron to the next free available inner/outer surface; and the internal formation of heavy nano-water droplets at nano-pores.

How does sustainable steel production through plasma smelting reduction work? Reduction based on a hydrogen plasma offers an attractive alternative to hydrogen-based direct reduction. In a set of experiments, we therefore studied the reduction of hematite using several types of hydrogen-containing plasmas [20,21,66,67]. The evolution of both, chemical composition and phase transformations were studied 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 towards 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 and atom probe tomography. Si-enrichment was observed in the interdendritic fayalite domains, at the wüstite/iron hetero-interfaces and in the oxide particles inside iron. With proceeding reduction, however, such elements are gradually removed 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.

# Can we turn toxic industry waste into a value-added

steel? We have recently shown that toxic waste can indeed be used as feedstock for green metallurgy, using the so-called 'red mud' as a model material. Red mud is the waste of bauxite refinement into alumina, the feedstock for aluminium production. With about 180 million tonnes produced per year, red mud has amassed to one of the largest environmentally hazardous waste products, with the staggering amount of 4 billion tonnes accumulated on a global scale. We therefore investigated how this red mud can be turned into valuable and sustainable feedstock for ironmaking using fossil-free hydrogen-plasma-based reduction, thus mitigating a part of the steel-related carbon dioxide emissions by making it available for the production of several hundred million tonnes of green steel [21]. The process proceeds through rapid liquid-state reduction, chemical partitioning, as well as density-driven and viscosity-driven separation between metal and oxides. We show the underlying chemical reactions, pH-neutralization processes and phase transformations during this surprisingly simple and fast reduction method. The approach establishes a sustainable toxic-waste treatment from aluminium production through using red mud as feedstock to mitigate greenhouse gas emissions from steelmaking.

Can we make high performance sheet steels from impurity-contaminated scrap? The sections above addressed sustainable primary synthesis methods to make green steel. However, secondary production (i.e. making new

allovs from impurity-contaminated scrap) are also essential domains for basic research. More specific, to counteract global warming, decarbonization of the steel sector must proceed much faster than the ongoing transition kinetics in primary steelmaking sketched above. Insufficient supply of green hydrogen is a particular bottleneck. Realizing a higher fraction of secondary steelmaking thus is gaining momentum as a sustainable alternative to primary production. Steel production from scrap is well established for long products (rails, bars, wire), but there are two main challenges. First, there is not sufficient scrap available to satisfy market needs. Today, only one-third of global steel demand can be met by secondary metallurgy using scrap since many steel products have a lifetime of several decades. However, scrap availability will increase to about two-thirds of total demand by 2050 such that this sector will grow massively in the next decades. Second, scrap is often too contaminated to produce high-performance sheet steels. This is a serious obstacle because advanced products demand explicit low-tolerance specifications for safety-critical and high-strength steels, such as for electric vehicles, energy conversion and grids, high-speed trains, sustainable buildings, and infrastructure. Therefore, we study the metallurgical and microstructural challenges and opportunities for producing high-performance sheet steels via secondary synthesis. Focus is placed on the thermodynamic, kinetic, chemical, and microstructural fundamentals as well as the effects of scrap-related impurities on steel properties.

# Can we make aluminium alloys from impurity-contami-

nated scrap? Recycling of aluminium shifts the CO<sub>2</sub> and energy balance of this material towards higher sustainability, because the energy needed to melt it from scrap is only about 5 % of that consumed in ore reduction. The amount of aluminium available for recycling is estimated to double by 2050. This offers an opportunity to bring the metallurgical sector closer to a circular economy. A challenge is that large amounts of scrap are post-consumer scrap, containing high levels of elemental contamination. This has to be taken into account in more sustainable alloy design strategies and requires to gain better understanding of how multiple scrap-related contaminant elements act on aluminium alloys and how future alloys can be designed upfront to become scrap-compatible and composition-tolerant [1]. We therefore explore the influence of scrap-related impurities on the thermodynamics and kinetics of precipitation reactions and their mechanical and electrochemical effects; impurity effects on precipitation-free zones around grain boundaries: their effects on casting microstructures; and the possibilities presented by adjusting processing parameters and the associated mechanical, functional, and chemical properties. The objective is to foster the design and production of aluminium alloys with the highest possible scrap fractions, using even low-quality scrap and scrap types which match only a few target alloys when recycled.

What is the role of microstructure in the recycling of hard magnets? Sintered Nd-Fe-B magnets industrially produced employing the grain boundary diffusion process (GBD) were recycled by the so-called functional or

short-loop recycling approach, based on hydrogen decrepitation (HD). Microstructural and magnetic differences between the original and the recycled materials were analysed. The functional recycling of GBD magnets leads to the dissolution of the core (heavy rare earth lean) - shell (heavy rare earth rich) structure through the different heat treatment steps which include hydrogen decrepitation, sintering, and annealing. The recycled magnets show similar rectangular demagnetization curves with squareness of 96 %, and only a slight decrease in remanence of 5 % to 1.31 T, but a larger decrease in coercivity of 21 % to 1703 kA/m. A new GBD step using a 1.5 wt.% pure Tb-foil leads again to the formation of a core-shell structure with 0.5 µm thick Tb-shells, which is similar to the microstructure of the original magnets prior to recycling. The coercivity of the recycled magnets is increased by 35 % from 1315 kA/m to 1780 kA/m at 50 °C and shows similar magnetic values as the original industrial magnets at 150 °C and 200 °C, respectively. The temperature coefficients for the remanence,  $\alpha$ , and for the coercivity,  $\beta$ , can also be fully restored and even exceed the original values which leads to an improved temperature stability of the recycled magnets compared to the original magnets.

# Part II: Protecting microstructures against hydrogen embrittlement.

How to modify the microstructure of steels to make them resistant against hydrogen embrittlement? The antagonism between strength and resistance to hydrogen embrittlement in metallic materials is an intrinsic obstacle to the design of lightweight yet reliable structural components operated in hydrogen-containing environments. To solve this problem, we developed a counterintuitive strategy to exploit the typically undesired chemical heterogeneity within the microstructures of steels. This effect leads to locally varying stability of the retained austenite against deformation-induced transformation [40,41,68,69]. It enables local enhancement of crack resistance and local hydrogen trapping. More specific, we use this approach in a manganese-containing highstrength steel and produce a high dispersion of manganese-rich zones within the microstructure. These solute-rich buffer regions allow for local micro-tuning of the phase stability, arresting hydrogen-induced microcracks and thus interrupting the percolation of hydrogen-assisted damage. This results in improved 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.

Can we make hydrogen resistant high-strength aluminium alloys? High-strength aluminium alloys help reduce the weight of automobiles, but are susceptible to environmental degradation. Hydrogen embrittlement is often indicated as the main culprit; however, the exact mechanisms underpinning failure are not understood: atomic-scale analysis of hydrogen inside an alloy remains a challenge, and this prevents deploying alloy design strategies to enhance the durability of the materials. We



performed near-atomic-scale analysis of H trapped in second-phase particles and at grain boundaries in highstrength 7xxx Al alloys [16,17]. We used these observations to guide atomistic *ab initio* calculations, which show that the co-segregation of alloying elements such as Mg or Zr and H favours grain boundary decohesion, and the strong partitioning of H into the second-phase particles removes solute H from the matrix, hence preventing H embrittlement. Our insights advance the mechanistic understanding of H-assisted embrittlement in Al alloys, emphasizing the role of H traps in minimizing cracking and guiding alloy design.

Can boron protect interfaces against hydrogen embrittlement of advanced high-strength steels? We investigated the interaction between boron and hydrogen at grain boundaries experimentally and numerically in boron-doped and boron-free martensitic steels using thermal desorption spectrometry (TDS) and ab initio calculations. The calculations show that boron, which mostly segregates into prior austenite grain boundaries (PAGBs), repels hydrogen. This behaviour has also been observed using TDS measurements, with the disappearance of one peak when boron is incorporated into the microstructure. Additionally, the microstructure of both boron-doped and boron-free steels has been studied through electron backscattered diffraction, electron channelling contrast imaging, synchrotron X-ray measurements, and atom probe tomography. While both steels have a similar grain size, grain boundary distribution, and dislocation densities, pronounced boron segregation into PAGBs is observed for boron doped steels. Therefore, the hydrogen concentration in different trapping sites has been evaluated using the Langmuir-McLean model. This thermodynamic model shows that all traps are filled identically when the total hydrogen concentration is low for boron-free steel. However, when it increases, traps of the lowest segregation energies (mostly PAGBs) are firstly saturated, which promotes failure initiation at this defect type. This finding partially explains why PAGBs are the weakest microstructure feature when martensitic steels are exposed to hydrogen-containing environments.

#### Part III: Magnetic materials

Microstructure Physics and Alloy Design Microstructure Physics and Alloy Design and an Alloy Design memory and an Alloy Design and an Alloy Design an Allo

Can we make mechanically strong and yet ductile soft magnets with extremely low coercivity? Soft magnetic materials (SMMs) serve in electrical applications and sustainable energy supply, allowing magnetic flux variation in response to changes in applied magnetic field, at low energy loss. The electrification of transport, households, and manufacturing leads to an increase in energy consumption owing to hysteresis losses. Therefore, minimizing coercivity, which scales these losses, is crucial. Yet meeting this target alone is not enough: SMMs in electrical engines must withstand severe mechanical loads; that is, the alloys need high strength and ductility. This is a basic design challenge, as most methods that enhance strength introduce stresses that can pin magnetic domains, thus increasing coercivity and hysteresis losses. We introduced a new approach to overcome this dilemma [14]. We have designed a Fe-Co-Ni-Ta-Al

multicomponent alloy (MCA) with ferromagnetic matrix and paramagnetic coherent nanoparticles (about 91 nm in size and around 55 % volume fraction). They impede dislocation motion, enhancing strength and ductility. Their small size, low coherency stress and small magnetostatic energy create an interaction volume below the magnetic domain wall width, leading to minimal domain wall pinning, thus maintaining the soft magnetic properties. The alloy has a tensile strength of 1,336 MPa at 54 % tensile elongation, extremely low coercivity of 78 A m<sup>-1</sup> (less than 1 Oe), moderate saturation magnetization of 100 A m<sup>2</sup> kg<sup>-1</sup> and high electrical resistivity of 103  $\mu$ 0 cm.

What is the role of dislocations in abnormal growth of Goss grains in grain-oriented electrical steels? The physical mechanisms that lead to the abnormal growth of Goss-oriented grains in grain-oriented electrical steel (GOES) are still not well understood, despite almost a century of research [70,71]. We therefore revisited all the existing hypotheses on the formation of Goss-oriented grains by abnormal grain growth and provided more insights into the underlying mechanism for Goss texture formation by proposing a new hypothesis referred to as "Dislocation-assisted particle dissolution" [43]. Abnormally grown Goss-oriented grains in fully-processed industrial GOES samples are shown to contain a fine network of internal subgrain boundaries with very low angle (0.03° - 0.18°) each consisting of regular arrays of dislocations. These subgrain boundaries form a branched ray-like pattern from the Goss grain centre towards its perimeter, i.e. they seem to have evolved with the grain during its growth. Structural and compositional analysis of these dislocations by controlled electron channelling contrast imaging (cECCI) and atom probe tomography (APT) show that these dislocations are enriched with solutes such as Sn. Cu. C. and more importantly, with Al. N. and Mn, which all build the composition of the inhibitor particles that assist the abnormal growth of Goss-oriented grains. Additionally, molecular statics (MS) calculations are employed to compare the segregation tendencies of AI atoms on dislocations and on Σ9 boundaries. It is found that AI prefers to segregate to dislocations rather than to the boundaries. The origin and the role of subgrain boundaries are discussed based on the experimental and simulation results. The results indicate that, after the dissolution of inhibitors along the grain boundaries, solutes are absorbed by the subgrain dislocations. As a result, grain boundaries surrounding Goss grains become less decorated by solutes and precipitates and more mobile compared to the boundaries of matrix grains.

**Can we design high temperature soft magnets?** Fast growth of sustainable energy production requires massive electrification of transport, industry, and households, with electrical motors as key components. These need soft magnets with high saturation magnetization, mechanical strength, and thermal stability to operate efficiently and safely. Reconciling these properties in one material is challenging because thermally-stable microstructures for strength increase conflict with magnetic performance. We developed a novel material design approach that combines thermal stability, soft magnetic

response, and high mechanical strength [72]. The strong and ductile soft ferromagnet is realized as a multicomponent alloy in which precipitates with a large aspect ratio form a Widmanstätten pattern. The material shows excellent magnetic and mechanical properties at high temperatures while the reference alloy with identical composition devoid of precipitates significantly loses its magnetization and strength at identical temperatures. This project provides a new avenue to develop soft magnets for high-temperature applications, enabling efficient use of sustainable electrical energy under harsh operating conditions.

What are promising trends for designing multi-functional high entropy materials? In a set of projects, we are generally concerned with identifying promising design targets for high entropy alloys. Entropy-related phase stabilization can enable compositionally complex solid solutions of multiple principal elements. The massive mixing approach was originally introduced for metals and has recently been extended to ionic, semiconductor, polymer, and low-dimensional materials. Multi-element mixing can leverage novel types of random, weakly ordered, clustering, and precipitation states in bulk materials as well as at interfaces and dislocations. The many possible atomic configurations offer opportunities to discover and exploit new functionalities, as well as create new local symmetry features, ordering phenomena, and interstitial configurations [73,74]. This opens up a huge chemical and structural space in which unchartered phase states, defect chemistries, mechanisms, and properties, some previously thought to be mutually exclusive, can be reconciled in one material [75]. Earlier research concentrated on mechanical properties such as strength, toughness, and ductility [76]. We shift the focus today therefore more towards multi-functional property profiles, including electronic, electrochemical, mechanical, magnetic, catalytic, hydrogen-related, Invar, and caloric characteristics. Opportunities lie in combining several of these features, rendering such materials multi-functional without sacrificing mechanical properties [5,14].

# Part IV: Simulation and artificial intelligence for material and process design.

Can we use active learning for Invar alloy discovery? Invar alloys have extremely low thermal expansion, making them attractive for several types of low temperature applications. Finding these types of alloys in a complex compositional space, however, is challenging. For this reason we developed an iterative scheme that combines machine learning, density functional theory, experiments, and thermodynamic calculation to find two new Invar alloys out of millions of candidates [5,77,78]. The alloys are compositionally complex so-called high entropy materials, thus demonstrating the power of this approach for materials discovery. More specific, high-entropy alloys which were used here as a versatile and chemically as well functionally well-tuneable alloy framework are solid solutions of multiple principal elements that are capable of reaching composition and property regimes inaccessible for dilute materials. Discovering those with valuable

properties, however, too often relies on serendipity, because thermodynamic alloy design rules alone often fail in high-dimensional composition spaces. We developed and applied an active learning strategy which is designed for lean data type problems to accelerate the design of high-entropy Invar alloys in a practically infinite compositional space based on very sparse data. Our approach works as a loop, integrating machine learning with density-functional theory, thermodynamic calculations, and experiments. After processing and characterizing 17 alloys out of millions of possible compositions, we identified two high-entropy Invar alloys with very low thermal expansion coefficients around 2 × 10<sup>-6</sup> per kelvin at 300 K. This opens up a suitable pathway for the automated discovery of high-entropy alloys with improved thermal, magnetic, and electrical properties (Fig. 9).



**Fig. 9:** Thermal expansion coefficient (TEC) as a function of temperature for 2 Invar alloys (TEC≈2×10<sup>-6</sup> K<sup>-1</sup>) and 2 Kovar alloys (TEC≈5×10<sup>-6</sup> K<sup>-1</sup>) we discovered, compared with HEAs and medium entropy alloys (MEAs). The new alloys show abnormally low TEC values compared to the HEAs, MEAs, and conventional alloys previously reported. Most Invar alloys show a low TEC but also low configurational entropy. The Invar alloys discovered in this work offer a good combination of low TEC and high configurational entropy. This indicates the high potential of the HEA concept for the design of Invar alloys, which, beyond their beneficial thermal expansion response, also offer high strength, ductility, and corrosion resistance [5].

Can we teach solid-state micro-mechanics to artificial intelligence? We developed methods to use artificial neural networks (specifically the U-Net neural network type) as surrogate models for the accelerated simulation of micromechanical problems in polycrystalline materials exposed to simple path-independent loading scenarios. More specific, we propose a deep neural network (DNN) as a fast surrogate model for local stress calculations in inhomogeneous non-linear materials [25,79,80]. We could show that the DNN predicts the local stresses with <4 % mean absolute percentage error for the case of heterogeneous elastic media and a mechanical contrast of up to factor of 1.5 among neighbouring crystal domains, while performing 10<sup>3</sup> times faster than spectral solvers. These DNN models have proven suited for reproducing the stress distribution in geometries different from those

used for training. In the case of elasto-plastic materials with up to 4 times mechanical contrast in yield stress among adjacent regions, the trained model simulates the micromechanics with an error of 6.4 % in one single forward evaluation of the network, without any iteration. The results reveal an efficient approach to solve non-linear mechanical problems, with an acceleration up to a factor of 8300 for elastic-plastic materials compared to conventional solvers. The approach is meanwhile also being further developed for more complex constitutive, thermal, and loading conditions.

Can we inversely design dual-phase steel microstructures using generative machine learning modelling? The design of optimal microstructures requires first, the identification of microstructural features that influence the material's properties and, then, a search for a combination of these features that give rise to desired properties [68]. For microstructures with complex morphologies, where the number of features is large, deriving these structure-property relationships is a challenging task [81]. To address this challenge, we propose a generative machine learning model that can automatically identify low-dimensional descriptors of microstructural features that can be used to establish structure-property relationships. Based on this model, the team developed an integrated, data-driven framework for microstructure characterization, reconstruction, and design that is applicable to heterogeneous materials with polycrystalline microstructures [62]. The proposed method is evaluated on a case study of designing dual-phase steel microstructures created with the multi-level Voronoi tessellation method. To this end, we train a variational autoencoder to identify the descriptors from these synthetic dual-phase steel microstructures. Subsequently, we employ Bayesian optimization to search for the optimal combination of the descriptors and generate microstructures with specific yield stress and low susceptibility for damage initiation. The results show how microstructure descriptors, determined by a variational autoencoder, act as design variables for an optimization algorithm that identifies microstructures with desired properties.

# Can we design ultrahigh-entropy alloys via text min-

Microstructure Physics and Alloy Design ing? It has long been the norm that researchers extract knowledge from literature to design materials. However, the avalanche of publications makes the norm challenging to follow. Text mining (TM) is an efficient approach in extracting information from corpora. Still, it cannot discover materials not present in the corpora, hindering its broader applications in exploring novel materials, such as high-entropy alloys (HEAs). In a series of projects, we developed and applied a concept of context similarity for selecting chemical elements for HEAs, based on TM models that analyse the abstracts of several million publications [25,82]. The method captures the similarity of chemical elements in the context used by scientists. It overcomes the limitations of TM and identifies the Cantor and Senkov HEAs. We demonstrate its screening capability for six- and seven-component lightweight HEAs by finding nearly 500 promising alloys out of 2.6 million candidates. The method thus brings an approach to the development of ultrahigh-entropy alloys and multicomponent materials.

Can we predict in-grain microstructural evolution by crystal plasticity simulations? We developed methods for high-resolution three-dimensional crystal plasticity simulations to investigate deformation heterogeneity and microstructure evolution during cold deformation of interstitial free (IF-) steels at microstructural scales. Our Fast Fourier Transform (FFT)-based spectral solver has been further developed to allow conducting complex crystal plasticity simulations using dislocation-density-based crystal plasticity constitutive formulations [60,83,84]. We found that the in-grain texture evolution and misorientation spread are consistent with experimental results obtained using electron backscatter diffraction (EBSD) experiments. The crystal plasticity simulations show that two types of strain localization features develop during the large strain deformation of IF-steel. The first type forms band-like areas with large strain accumulation that appear as river patterns across the specimen. In addition to these river-like patterns, a second type of strain localization with rather sharp and highly localized in-grain shear bands is identified. These localized features are dependent on the orientation of the grain and extend within a single grain. In addition to strain localization, the evolution of in-grain orientation gradients, misorientation features, dislocation density, kernel average misorientation, and stress in major texture components are revealed.

How can we accelerate the design of compositionally complex materials via physics-informed artificial intelligence? The chemical space for designing materials is practically infinite. This makes disruptive progress by traditional physics-based modelling alone challenging. Yet, training data for identifying composition-structureproperty relations by artificial intelligence are sparse. We develop opportunities to discover new chemically complex materials by hybrid methods where physics laws are combined with artificial intelligence. We extracted from this a set of questions and solution strategies to pursue in the coming years [5,25,85]. These include the question how can AI methods be trained with sparse and noisy data in materials science? One approach we pursue involves using (1) existing thermodynamic and kinetic databases; (2) combinatorial high-throughput experimental methods to create extensive material libraries with automated characterization and active-learning experiments; (3) massive forward simulations; and/or (4) automated language processing and advanced word embedding methods to improve databases and training sets. Further, how can AI methods for designing complex alloys be integrated with physics-based models? Promising approaches include data-driven surrogates of physical models, physically informed neural networks, and operator learning, which can accelerate material response and property calculations. Even data-driven models can extrapolate beyond training data in microstructure, mechanics, damage, and topology. AI methods can partially replace classical computational methods, allowing the exploration of material candidate spaces much larger than currently possible. Next, we will study what are suitable

descriptors for linking complex chemical compositions to properties? While simulation methods to relate compositions and microstructures to properties are established, identifying suitable descriptors from machine learning or hybrid methods needs more study. Various approaches to 'featurize' composition and material data exist, but composition-to-property linkage requires comprehensive information. Natural language processing could be useful in automatically extracting suitable descriptors from publications, forming a pillar of AI-based material discovery and design strategies. A further aspect is how the vast existing phenomenological knowledge can be screened and exploited using automated data retrieval with word embedding methods? Challenges include copyright issues, restricted access, and diverse nomenclatures and notations. Information quality varies, particularly regarding details like impurity content and microstructure features. Subtle effects from elements such as hydrogen, nitrogen, and carbon are important in materials like metallic high-entropy alloys. Reliable composition-structure-property relationships are vital. Another point is what methods can assist to avoid overlooking interesting outliers in the huge composition space? Outliers may be sources of real discoveries, while expected trends may be less exciting. Determining the best hybrid method or machine learning approach to discover truly novel materials is crucial. Some possible approaches using machine learning for material discovery are already in the literature. We also pursue strategies how AI can guide material discovery. AI can help decide specific research directions, making autonomous decisions about promising chemical subspaces. Deep-learning and active-learning strategies need further exploration to guide searches into composition subspaces without researcher bias. A generally weak point of AI in material design in this respect is insufficient consideration of unplanned elemental intrusion and associated compositional variations from synthesis and recycling. This will impact material design and must be addressed, along with life-cycle assessment constraints, to make AI more holistic and sustainable. Despite diverse AI approaches used in the field, no clear best-practice method trends are discernible as yet. The reasons behind the success of certain AI methods in addressing challenges associated with complex materials are not yet fully understood. Understanding these reasons may open pathways to custom designing modelling tools for future material design.

Despite these challenges, AI is expected to play a significant role in understanding and designing compositionally complex materials, driven by the fast development of Al algorithms, availability of high-quality datasets, and high-performance computing resources.

### Can we conduct corrosion research by deep learning and use of large language models? In a few recent projects,

we studied the possibility of using methods from artificial intelligence for corrosion research [23,85]. We have for instance developed a deep-learning-based framework for understanding the individual and mutually combined contributions of different alloying elements and environmental conditions towards the pitting resistance of corrosion-resistant alloys. A deep neural network (DNN) was trained on previously published datasets on corrosion-relevant electrochemical metrics, to predict the pitting potential of an alloy, given the chemical composition and environmental conditions. Mean absolute error of 170 mV in the predicted pitting potential, with an R-square coefficient of 0.61 was obtained after training. The trained DNN model was used for multi-dimensional gradient descent optimization to search for conditions maximizing the pitting potential. Among environmental variables, chloride-ion concentration was universally found to be detrimental. Increasing the amounts of dissolved nitrogen/ carbon was found to have the strongest beneficial influence in many alloys. Supersaturating transition metal high entropy alloys with large amounts of interstitial nitrogen/ carbon emerged as a possible direction for corrosion-resistant allov design [23].

Furthermore, we also proposed strategies that couple natural language processing with deep learning to enhance machine capability for corrosion-resistant alloy design [23,85]. First, accuracy of machine learning models for materials datasets is often limited by their inability to incorporate textual data. Manual extraction of numerical parameters from descriptions of alloy processing or experimental methodology inevitably leads to a reduction in information density. To overcome this, we have developed a fully automated natural language processing approach to transform textual data into a form compatible for feeding into a deep neural network. This approach has resulted in a pitting potential prediction accuracy substantially beyond state of the art. Second, we have implemented a deep learning model with a transformed-input feature space, consisting of a set of elemental physical/chemical property-based numerical descriptors of alloys replacing alloy compositions. This helped in the identification of those descriptors that are most critical toward enhancing the pitting potential. In particular, configurational entropy, atomic packing efficiency, local electronegativity differences, and atomic radii differences proved to be the most critical.

## Part V: The interplay of chemistry, mechanics and microstructure.

What is the role of chemo-mechanical failure mechanisms of the silicon anode in solid-state batteries? Silicon is a promising anode material due to its high theoretical specific capacity, low lithiation potential and low lithium dendrite risk. Yet, the electrochemical performance of silicon anodes in solid-state batteries is still poor (for example, low actual specific capacity and fast capacity decay), hindering practical applications [39]. We revealed the chemo-mechanical failure mechanisms of composite SilLi6PS5Cl and solid-electrolyte-free silicon anodes by combining structural and chemical characterizations with theoretical simulations. The growth of the solid electrolyte interphase at the SilLi6PS5Cl interface causes severe resistance increase in composite anodes, explaining their fast capacity decay. Solid-electrolyte-free silicon anodes show sufficient ionic and electronic conductivities, enabling a high specific capacity. However, microscale void formation during delithiation causes larger mechanical

stress at the two-dimensional interfaces of these anodes than in composite anodes. Understanding these chemo-mechanical failure mechanisms of different anode architectures and the role of interphase formation helps to provide guidelines for the design of improved electrode materials.

Can we observe the degradation of a Si anode in a Liion battery at the atomic scale? To advance the understanding of the degradation of the liquid electrolyte and Si electrode, and their interface, we exploited the latest developments in cryo-atom probe tomography [29,86-89]. We evidence Si anode corrosion from the decomposition of the Li salt before charge-discharge cycles even begin [30]. Volume shrinkage during delithiation leads to the development of nanograins from recrystallization in regions left amorphous by the lithiation. The newly created grain boundaries facilitate pulverization of nanoscale Si fragments. P is segregated to these grain boundaries, which confirms the decomposition of the electrolyte. As structural defects are bound to assist the nucleation of Li-rich phases in subsequent lithiation and accelerate the electrolyte's decomposition, these insights into the evolving microstructure interacting with the electrolyte contribute to understanding the self-catalyzed/accelerated degradation of Si anodes and can inform new battery designs unaffected by these life-limiting factors.

Can we improve electrocatalysts through engineering impurities? Fuel cells recombine water from H<sub>2</sub> and O<sub>3</sub> thereby can power, for example, cars or houses without local carbon emission. In anion-exchange membrane fuel cells (AEMFCs), to reach high power densities, operating at high pH is an alternative to using large volumes of noble metals catalysts at the cathode, where the oxygen-reduction reaction occurs. However, the sluggish kinetics of the hydrogen-oxidation reaction (HOR) hinders upscaling despite promising catalysts. We now observed an unexpected ingress of B into Pd nanocatalysts synthesized by wet-chemistry, gained control over this B-doping, and can even detect its influence on the HOR activity in alkaline conditions [33]. The findings were rationalized using ab initio calculations of both H- and OH-adsorption on B-doped Pd. Using this "impurity engineering" approach, they thus design Pt-free catalysts as required in electrochemical energy conversion devices, for example, next generations of AEMFCs, that satisfy the economic and environmental constraints, that is, reasonable operating costs and longterm stability, to enable the "hydrogen economy".

How to model oxide reduction by chemo-mechanical-

ly coupled phase-field models? Along the context of

sustainable metallurgy outlined above, we developed a

chemo-mechanically coupled phase-field model further

to explore the interplay between phase transformation,

chemical reaction, species diffusion, large elasto-plas-

tic deformation and microstructure evolution, such as

occurring in the fields of reduction, oxidation, and batter-

ies [6,90-92]. In a set of projects devoted specifically to

green steel production by using hydrogen as a reductant,

the energetic constitutive relations of the model are based

on the system's free energy which is calibrated with the

f these anodes ng these che-ifferent anode ormation helps oved electrode
anode in a Li-anode in a Li-anote the under-ectrolyte and Si
d the latest de-bhy [29,86–89].
decomposition cles even begin
help of a thermodynamic database for the system Fe-0 [6]. The model has been first applied to the classical coreshell (wüstite-iron) structure. Simulations show that the phase transformation from wüstite to iron can result in high stresses and rapidly decelerating reaction kinetics. Mechanical stresses create elastic energy in the system, an effect which can negatively influence the phase transformation. However, if the elastic stress becomes comparatively high, it can shift the shape of the free energy from a double-well to a single-well case, speed up the transformation, and result in a higher reduction degree compared to the low-stress double-well case. The model has been applied to simulate an experimentally character-

has been applied to simulate an experimentally characterized iron oxide specimen with its complex microstructure. The observed microstructure evolution during reduction is well predicted by the model. The simulation results also show that isolated pores in the microstructure are filled with water vapor during reduction, which can influence the local reaction atmosphere and dynamics.

Can we inspect frozen water at near-atomic-scale? Transmission electron microscopy went through a revolution enabling routine cryo-imaging of biological and (bio)chemical systems, in liquid form. Yet, these approaches typically lack advanced analytical capabilities. Here, we used atom probe tomography to analyse frozen liquids in three dimensions with subnanometre resolution [29]. We introduce a specimen preparation strategy using nanoporous gold. We conducted experiments on 2- to 3-µm-thick layers of ice formed from both high-purity deuterated water and a solution of 50 mM NaCl in high-purity deuterated water. The analysis of the goldice interface reveals a substantial increase in the solute concentrations across the interface. We then explored a range of experimental parameters to show that atom probe tomography analyses of bulk aqueous specimens come with their own challenges and discussed physical processes that produce the observed phenomena. Our study demonstrates the viability of using frozen water as a carrier for near-atomic-scale analysis of objects in solution by atom probe tomography.

How do atomic motifs govern the decoration of grain **boundaries by interstitial solutes?** Several projects were concerned with studying the interplay of segregating elements and the structural features of grain boundaries (and phase boundaries) at the atomic scale [17,93-96]. Grain boundaries, the two-dimensional defects between differently oriented crystals, tend to preferentially attract solutes for segregation. Solute segregation has a significant effect on the mechanical and transport properties of materials. At the atomic level, however, the interplay of structure and composition of grain boundaries remains elusive, especially with respect to light interstitial solutes like B and C. Here, we use Fe alloyed with B and C to exploit the strong interdependence of interface structure and chemistry via charge-density imaging and atom probe tomography methods. Direct imaging and quantifying of light interstitial solutes at grain boundaries provide insight into decoration tendencies governed by atomic motifs. We find that even a change in the inclination of

the grain boundary plane with identical misorientation impacts grain boundary composition and atomic arrangement. Thus, it is the smallest structural hierarchical level, the atomic motifs, that controls the most important chemical properties of the grain boundaries. This insight not only closes a missing link between the structure and chemical composition of such defects but also enables the targeted design and passivation of the chemical state of grain boundaries to free them from their role as entry gates for corrosion, hydrogen embrittlement, or mechanical failure.

What is the structure dependence of the chemical decoration of dislocations? Little is known at the near-atomic scale about the interplay of dislocations of different type and the 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 atomic-scale characterization methods have made it possible to quantitatively resolve defect types and segregation chemistry. For a Pt-Au model alloy, we observe a wide range of defect-specific solute (Au) decoration patterns of much greater variety and complexity than expected from the Cottrell cloud picture [97]. 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 use dislocations for the compositional and structural nanoscale design of advanced materials.

What is the effect of Re in Ni-based superalloys? Single crystal Ni-based superalloys have long been an essential material for gas turbines in aero engines and power plants due to their outstanding high temperature creep, fatigue. and oxidation resistance. A turning point was the addition of only 3 wt.% Re in the second generation of single crystal Ni-based superalloys which almost doubled the creep lifetime. Despite the significance of this improvement, the mechanisms underlying the so-called "Re effect" have remained controversial. We provided evidence of Re enrichment to crystalline defects formed during creep, using combined transmission electron microscopy, atom probe tomography, and phase field modelling [98]. We reveal that Re enriches to partial dislocations and imposes a drag effect on dislocation movement, thus reducing the creep strain rate and thereby improving creep properties. These insights can guide design of better superalloys, a quest which is key to reducing CO<sub>2</sub> emissions in air-traffic.

# Low-dimensional thermodynamics and kinetics at lattice defect

Projects in this topical field deal with the understanding and local chemical manipulation of individual lattice defects. These features, such as dislocations and grain boundaries, influence mechanical, functional, and kinetic properties 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, cohesion and can even promote local phase transformation [4,99-103]. In an approach referred to as 'segregation engineering' such solute decoration is not regarded as an undesired phenomenon, but it is instead utilized to manipulate specific defect structures and properties via local composition tuning. 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. In a Pt-Au model alloy we observed 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 guenched 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.

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Microstructure Physics and Alloy Design

Microstructure

Physics and

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Design





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

G. Dehm

# Scientific mission and concepts

**Mission:** We perform cutting-edge basic research to understand the relationships between synthesis, microstructure and properties to enable reliable, efficient, and novel material applications. Our research is focussed on metals, complex alloys, intermetallic materials and protective coatings. The synthesis methods we apply depend on the research mission and include amongst others additive manufacturing, diffusion couples and physical vapour deposition. For micro-architectured materials we develop novel approaches using 3-dimensional (3D) micro-printing [1,2], a new research topic supported since 2023 by an ERC Starting Grant (R. Ramachandramoorthy) allowing to print complex (auxetic) lattices, MEMS devices but also to encapsulate liquids (see p. 57).

We have a strong research focus on **mechanical properties at the microstructural length scale** [3-27] as they are critical to the sustainability of materials. They are an important aspect that determines how well materials can adapt to harsh conditions, which has a direct impact on their durability. This requires the development of novel testing set-ups [2,28], which operate at variable strain rates, temperatures and environments and deliver quantitative data. We have in the last years developed nanoindentation tools and test protocols allowing to achieve so far unreached strain rates of up to  $10^5 \, \text{s}^{-1}$ , to operate at  $1000^{\circ}$ C down to cryogenic temperatures, and to perform site specific nano-/micromechanical testing *in situ* under hydrogen charging and de-charging conditions.

Along the micro- and nanometre length scales of the same materials and down to the atomic level, we aim at a **coherent understanding of the microstructure, its evolu-tion and internal atomic scale imperfections along with their thermodynamic stability and kinetics** [4,27,29-65]. This is accomplished by aberration corrected scanning transmission electron microscopy (STEM) methods, which are often further developed in-house to meet our request. We have developed our own Python-based tool-box for fast and reliable template matching in orientation mapping, a novel MEMS device for *in situ* straining in the S/TEM, and with collaboration partners schemes for au-tomated feature recognition and extraction [31,42,48].

Our understanding of atomic scale defects and their defect phases (sometimes called "complexions") such as for grain boundaries [27,32,36-38,40,41,45], but also stacking faults [54,62,66], dislocations [17,28,66-69] and point defects [4,39] has advanced by combining atomic scale characterization with atomistic simulations [30, 32,36,38,40,70-72] and often complemented by nano/

micromechanical [6,11,13, 5] or local electrical measurements [4,7,12,17,18,22,70,73,74]. Such insights are important for finding design strategies to resolve embrittlement e.g. by liquid metals [27,37,51], impurities [6,35] or hydrogen [28,69,75-77], but also to understand dislocation – grain boundary interactions [11,13,15] as they are important for strength and ductility of a material. Furthermore, grain boundaries and dislocations and their possible thermodynamic defect phase transitions are at the core of our research as their fundamentals are poorly understood, but may have significant impact on electrical and mechanical properties. These activities were also supported by an ERC Advanced Grant (G. Dehm) and [15,17,22,30,32, 36,38,40,45,56,57,70,72, see p. 54].

Looking ahead, we are expanding our research mission towards energy related materials, where (chemo-) mechanical properties are a limiting or become the critical factor for functionality, safety and longevity. Examples are materials for a hydrogen infrastructure as well as battery materials. For solid-state batteries. Lithium (dendrite) growth through inorganic solid electrolytes is a phenomenon resembling similarities to crack propagation. It needs a fundamental understanding of internal stresses and mechanical properties of the constituent materials, their phases and defect (phases) to be able to provide design strategies to overcome this critical issue causing safety hazards and failure. The required dedicated workflows, environments and novel test methods are currently buildup in the SN department.

Novel test methods are also developed to tackle all aspects of hydrogen impact on materials [28,69,75-77]. A new environmental SEM has been installed in 2024, which is dedicated for microstructure analyses and site-specific "nano-/micro- mechanical microscopy" under specific gas atmospheres including hydrogen. In 2026 we will receive a world-wide unique environmental STEM, where we can combine atomic scale investigations under hydrogen gas exposure (~20 Pa) with external stimuli (temperature, strain, electrical current, ..) and ultra-high resolution spectroscopy (>6meV) allowing to probe phonons site specifically at selected nano-/microstructure features. This will for example shed light on how defects are decorated with hydrogen (e.g. dislocation cores, formation of first hydride nuclei, etc.) and how this will impact their mobility and multiplication under external stimulus using in situ MEMS straining within the same unique instruMAX PLANCK INSTITUTE

ment. A new research group will be established to get this exciting endeavour started (see p. 51).

Department structure and laboratories: The department structure consists currently of 6 groups. The group Advanced Transmission Electron Microscopy (C. Liebscher until 03/2024; P. Schweitzer since 11/2024) performs cutting edge research using a plethora of STEM methods such as 4D STEM, orientation mapping, atomic resolved imaging and spectroscopy to unveil the internal atomistic structure of complex defects in mainly metals, alloys and intermetallic materials. An aberration corrected STEM (installed 2014) with electron energy-loss-spectroscopy, an aberration corrected TEM with EDS (2016) are the core of our high-end instruments. They are complemented by a conventional TEM (2019) and a field emission S/TEM (2006) mainly dedicated to orientation mapping and in situ experiments. Our portfolio of dedicated in situ holders allows for mechanical, electrical, and thermal, or electrochemical stimuli. In 2026, we will receive our unique environmental STEM for complex in situ experiments and ultimate energy resolution electron energy-loss spectroscopy. A new group Environmental and Analytical Electron Microscopy, led by L. Vogl was founded in 11/2024, which will tackle the detection of hydrogen at material defects and their impact on material properties. Our quantitative "nano-/micromechanical microscopy" is subdivided in three groups: The group Extreme Nanomechanics (R. Ramachandramoorthy) focusses strongly on method development for ultra-high strain rates (currently 10<sup>5</sup> s<sup>-1</sup>) and variable temperature (30 K to 1300 K). The group Mechanics at Chemical Interfaces (J. Best until 12/2024) deals with a basic understanding of the mechanical properties of and at internal defects, such as brittle to ductile transitions of hetero-interphases. The permanent group Hydrogen Mechanics at Interfaces (J. Duarte) studies the complex cosmos of hydrogen-microstructure interactions in materials. Several in situ nanoindentation based platforms are available and further developed for the specific research tasks of the different groups. A focussed ion beam FIB-SEM (2012), a dedicated in situ SEM (2017) and an environmental SEM (2024) are essential for the smallscale mechanical experiments. Since its start in 2012, the SN department hosts the permanent group Intermetallic Materials (M. Palm, F. Stein), which contributes with it expertise on constitution, thermodynamics and mechanical properties to the mission of the SN department and operates the institute's thermodynamic laboratory.

The third party funded group **Atomistic Modelling of Material Interfaces** (T. Brink) plays a vital role in advancing our understanding of defect kinetics and thermodynamics. The group fruitfully und mutually interacts with our advanced STEM and nano-/micromechanical testing experts and was created out of G. Dehm's ERC Advanced Grant. Another third party funded temporary group deals with micro-additive manufacturing of miniaturized structures with unmatched degrees of freedom for printing complex 3D structures, as well as novel MEMS and mechanical devices. This group is headed by R. Ramachandramoorthy and financed by the ERC Starting Grant AM-Micro (see p. 57). **Personal development, careers and awards:** Career development is a strong aspect in the SN department. We offer personal interview trainings, external soft skill courses, and participate successfully in the MPG "Sign Up! Careerbuilding" program directed to female scientists and their needs. In addition, several female department members were selected for the dedicated MPI-SusMat mentoring program (see p. 114).

The high visibility of our scientists is mirrored by high-level academic appointments. C. Liebscher was appointed full professor in physics (2024) at the Ruhr University Bochum (RUB), C. Kirchlechner in materials science at Karlsruhe Institute of Technology (2020). Former Humboldt postdoc H. Bishara joined Tel Aviv University as a faculty (2022), and several former group members became or continued faculty positions in Slovenia (J. Zavašnik), China (Wenzhen Xia; Wenjun Lu, Degang Xie, Ningyan Cheng), South Korea (S.G. Kang) and India (M. Kini). Several Humboldt postdocs worked in the report period 2022-2024 with us: Ningvan Cheng (jointly with NG), Xuyang Zhou (jointly with MA), Barbara Bellon, Dipali Sonawane, Degang Xie. Cleiton Carvalho Silva from Brazil received a Capes-Humboldt Research Fellowship (2021-2022). Due to the pandemic our Friedrich Wilhelm Bessel Award winner Y. Zhu (2020) from North Carolina State University and Humboldt award winner Dominique Chatain (2020), a CNRS director at CINAM Marseille, were only able to visit us 2 years after receiving their awards. Furthermore, S.G. Kang was awarded a NRF scholarship (National Research Fund of Korea) and B. Bellon a Marie-Curie Intra-European Fellowship. 5-year Max-Planck Partner groups (see p. 40,43,46) were awarded by the MPG in a competitive process to J. Zavašnik (2021). H. Bishara (2023) and S.G. Kang (2024) fostering our collaborations on materials in extreme environments, electrical property modifications caused by atomic scale defects, and sensitivity of materials' mechanical properties to electron beam exposure.

We host regularly summer students from Cambridge University, UK. In 2023, Piotr Sokolinski received the prestigious European Placement Prize of Cambridge University. Dong-jin Lee (2023) and Yoonji Choi (2024) from South Korea were awarded with a Korea-German Junior Research Fellowship by Max Planck Korea. For his excellent PhD, B. Distl received the Otto Hahn Medal of the Max Planck Society (2023). J. Best was in 2023 awarded with the Georg-Sachs-Prize (see p. 61) of the German Materials Society DGM for his outstanding work on the chemo-mechanical properties in modern structural and functional materials. A further highlight was the 2022 ERC Starting Grant for R. Ramachandramoorthy with a value of 1.5 Mio Euro dedicated to research on additive micro-manufacturing. The Intermetallic Materials group around F. Stein received best paper awards in 2022 and 2023, and F. Stein for his review paper on Laves phases in 2022 the William Bonfield Prize.

Third party research projects: We are very active in several DFG funded Collaborative Research Centres, which are aligned with the department's research mission. This

includes the SPP 2006 Compositionally Complex Allovs - High Entropy Alloys (2018-2024), the SFB 1394 Structural and Chemical Atomic Complexity: From Defect Phase Diagrams to Material Properties (2020-2026), and the TRR188 Damage Controlled Forming Processes (2018-2024) (see p. 82,84,89). Several projects funded by the European Union including the ERC Starting Grant AM-Micro, ERC Advanced Grant GB-CORRELATE, Eurostars project HINT (see p. 57,54,85), the project ADVANCE (see p. 87), and the hydrogen related project HyWay (see p. 103), are running in the report period 2022-2024. Within the Max Planck Society we were actively participating in the large network initiative Big Data Driven Materials Science (see p. 83) and the program for external partner groups (see p. 40,43,46). Our hydrogen activities are partly supported by the projects H2BS and HEPCO (see p. 92) funded by the German Federal Ministry for Economic Affairs and Climate Action, and the KSB Foundation. Several DFG-funded projects complement our competitively raised third-party funds, which enhance our research portfolio and contribute to the academic career development of our principal investigators.

**Community service and teaching:** We have (co-)organized several workshops and conferences in the last years. This includes annual symposia in USA at the International Conference on Metallurgical Coatings and Thin Films-ICMCTF (J. Duarte), the conference Intermetallics 2023 (F. Stein), the annual MSIT Winter School on Materials Chemistry (M. Palm, F. Stein), the BiGmax Workshop on Big-Data-Driven Materials Science 2022 (G. Dehm, J. Neugebauer), the joint SN&NG annual conference series Mechanics Meets Energy (G. Dehm, C. Scheu, see Fig. 1), symposia metals and alloys at the Microscopy Conference 2023 and the European Microscopy Society 2024 (G. Dehm), and the symposium Experimental Micromechanics and Nanomechanics at 11<sup>th</sup> European Solid Mechanics Conference ESMC2022 (G. Dehm) to present some highlight examples.

In addition, we are active in dissemination of our results at conferences, using modern media including webinars, science slams and interviews. Our research also enters into our courses, which are taught at the RUB on "mechanical properties of materials at small dimensions" and "advanced transmission electron microscopy" for the curriculum materials science. Our early career researchers contribute with dedicated lectures and exercises to the success of these courses. G. Dehm and C. Scheu with the support of S. Zhang and C. Liebscher also taught annually a course on atomic scale characterization of materials at the curriculum physics at Heinrich Heine University in Düsseldorf. G. Dehm serves since 2017 the Humboldt Foundation as an expert evaluator in the committee for postdoctoral scholarships, was active in the board of governors of Acta Materialia Inc., and is a member in the selection committees for the Lise Meitner program and the independent research group leader program of the MPG. Furthermore, SN team members serve as evaluators for international journals, several international funding agencies, universities, and research institutions.



Fig. 1: The SN and NG department retreat in January 2024.

# Main scientific breakthroughs

Our research is focused on uncovering fundamental aspects of materials science that in some cases are also highly relevant to our modern societal needs in an ever-changing world. Our main breakthroughs are related to:

# (i) Hydrogen embrittlement mechanisms and its prevention

(ii) Advanced novel materials for sustainable use (iii) Grain boundary phases and their impact on properties (iv) Advancing miniaturized testing and its application for a mechanism-based understanding of materials

(i) Our main breakthrough in understanding **hydrogen embrittlement** is closely related to our self-build, novel back-side charging electrochemical cell integrated in a nanoindentation system [28,69,81]. With this set-up, we have found, that the hardness within a single grain of bcc FeCr alloys is directly related to the amount of diffusible

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hydrogen and increases with increasing hydrogen content [81]. This hardness increase is directly related to a higher dislocation density and a higher frictional stress for dislocation motion. Furthermore, the raising and falling hardness signal with time during hydrogen charging and release is so sensitive to the hydrogen content that it allows to give precise estimates of the hydrogen diffusion coefficient [81]. This was confirmed by Kelvin probe measurements. In a next step we will tackle the cohesive strength of grain boundaries with and without hydrogen. As a hydrogen embrittlement prevention mechanism, barrier coatings are a viable strategy. We analysed Al<sub>2</sub>O<sub>2</sub> barrier coatings applied directly or with an Al adhesion promoting layer on FeCr alloys [75,76]. The hydrogen diffusion rate in the amorphous Al<sub>2</sub>O<sub>2</sub> barrier coating was found to be 9 orders of magnitude lower than for the FeCr alloy and no microstructural or mechanical degradation was found for the barrier coating and the interface to the steel substrate [76,77]. In contrast, the Al adhesion layer revealed to be detrimental in case of long term elevated temperature exposure (200 °C or higher) as the Al layer slowly dewets below the barrier coating causing blisters independent of the gas environment [75]. Thus, stability against thermally induced dewetting needs to be considered for adhesion promoting layers if used at temperatures >  $\sim 0.4 T_{melt}$ .

(ii) The portfolio of advanced materials includes from FeAl based alloys with superior high temperature strength by forming metastable Heusler phases in the grain interior and fine scaled Laves phases at the grain boundaries [82]. Nb and especially Ta are very promising alloving additions to accomplish such dedicated microstructures suitable for light-weight, oxidation and creep resistant applications such as in turbines. This material system has been tackled by us from synthesis, constitution, microstructure characterization, micro-mechanical studies to bulk mechanical testing over the years [82-86]. A similar success story are TiAl based light-weight alloys promising a reduction in weight and higher operating temperatures for turbine blades in aero engines. For this material class we focused on constitution and materials characterization to suggest superior compositions based on our newly established ternary Ti-Al-X (X= Nb, Mo, W, Zr, Si, and O) phase diagrams [87-94]. Our systematic studies of high entropy alloys (or chemically complex alloys) led to a breakthrough in obtaining a homogenously, particle reinforced alloy by additive manufacturing [65,95]. Currently, we study the resistance against hydrogen ingress and embrittlement as preliminary nanoindentation measurements indicate hydrogen tolerance. Further breakthroughs in materials are achieved for thin film structures. We have successfully developed strategies to make brittle films more damage tolerant [96-99], and metallic glass thin films more ductile by either changing the chemical composition [22-24] or incorporating multiple interfaces [16,19,100]. In addition, we also shed light on the temperature dependent electrical resistivity of metallic glass thin films [22].

(iii) We have found that grain boundary phase transitions ("complexions") are unexpectedly a common phenomena even in pure fcc metals based on multiple and detailed atomic resolved experiments for Cu [40.56] and Al [32,38], and numerous atomistic simulations for fcc metals [30.32.38.40.71.72]. The packing density of atoms at the grain boundary and the bonding interactions up to the second nearest neighbours are the most important parameters determining the evolving grain boundary structure units as a function of temperatures and stress [71]. Upon segregation, differences in structural units can occur: for Zr the structure motifs of the grain boundary get more randomized as found for  $\Sigma$ 19b <111> tilt grain boundaries in CuZr alloys [57], with decoration starting first at disconnections. In contrast, Ag modifies the grain boundary structure units and fills certain places first [36,45]. Electrical resistivity of grain boundaries depends strongly on the excess volume as found for Cu tilt grain boundaries. However, the impact of different inclinations and atomic structure motifs are beyond the resolution limits of our unique electrical measurement protocols [70]. In contrast, dilute segregation leads to a measurable change of grain boundary resistivity as for the case of Cu containing trace levels of Fe [12].

For the formation of disconnections, the structural units play an important role as they can exclude some Burgers vectors and step heights in case they do not match with the repeat units of the structural grain boundary motifs as found by atomistic simulations [72]. The gained fundamental knowledge on grain boundary atomistics is not only of academic interest, but has important consequences for grain growth, shear coupled grain boundary motion and applications of metallization and conduction lines in semiconductor devices.

(iv) Our basic research on small scale mechanical testing has provided us with tools for compression, tension, and shear deformation, bending, fracture, interface shear and tribological [101] tests at the micro- and submicrometre length scales [102]. Several of these tests were pioneered by us and with our new additive micro-printing device we realize custom-made designs such as localized shear tests, which will even work for in situ TEM studies. The newly self-designed and printed micro-/nano-devices as well as MEMS emerging from our collaboration with Humboldt Bessel Award winner Y. Zhu (North Carolina State University) are currently explored and led to first result. Due to the successful application of the small scale "mechanical microscopy" we have shed light on brittle to ductile transition of Laves phases [3] difficult to test flawless in bulk conditions, or dislocation - grain boundary transmission mechanisms [11,15,79] to name two prominent examples. For the latter, our tests were so sensitive that we could even discriminate between different mechanisms for dislocation transmission through a twin grain boundary [15]. Also very unique are our integrated back-side charging electrochemical cell [28] and nanomechanical testing solutions for strain rates up to 10<sup>5</sup> s<sup>-1</sup> for nanoindentation and 10<sup>3</sup> s<sup>-1</sup> for micro-compression testing enabling us to explore new material physics.

# Scientific groups

Advanced Transmission Electron Microscopy (C. Liebscher [until 03/2024], P. Schweitzer [since 11/2024])

## Group mission

The overall mission of the Advanced Transmission Electron Microscopy (ATEM) group is to develop and advance modern techniques in the transmission electron microscope (TEM) with the aim to understand and explore the micro- and nanostructure of complex interfaces and materials. The goal is to resolve how a material is structured from the atomic level to mesoscopic length-scales and to being able to observe how the material behaves when exposing it to external stimuli. This enables to establish fundamental structure-property relationships needed to advance our understanding of material functionality.

From a technique development side, we have further extended the capabilities of 4D-scanning TEM (STEM) methods to perform automated crystal orientation mapping using open-source toolboxes [42], determine the 3D orientation of crystals in nanocrystalline materials [103] and to image light solute elements in grain boundaries [27] as shown in Fig. 2. We are currently combining 4D-STEM with *in situ* probing techniques to establish quantitative insights into material behaviour and function (see Fig. 2d) [29]. We further advance *in situ* capabilities in the S/TEM to explore interface transformations at elevated temperatures, to observe phase transformations down to cryogenic temperatures and probe material deformation processes at atomic resolution.

The atomic scale imaging, 4D-STEM and *in situ* methods are applied to study the correlation of the structure, composition and properties of grain boundaries in elemental and multicomponent metallic materials [32,36-38,51,104]. In the past years, the ATEM group has been extending the exploration of structure-property relationships beyond mechanical properties [35,43,105] to soft-magnetic [29,34] and catalytically active materials [106]. In ongoing work, we investigate the intrinsic structure of complex oxide compounds focusing to resolve miniscule deviations in oxygen octahedral tilting using atomic resolution electron ptychography (see Fig. 2f).

Besides mere experimental work and technique development, the ATEM group has been leading broad efforts in advancing computational data analysis approaches and applying machine learning techniques to microscopy data, partly supported by the BiGmax initiative of the MPG [31,42,107]. We have developed a Bayesian convolutional neural network, which is capable to automatically classify crystal structures in atomic resolution images and even identify out-of-distribution features, such as interfaces, by considering the uncertainty distribution in the prediction [107].



**Fig. 2:** a) Example of open-source based crystal orientation mapping (pyxem) of nanocrystalline Cu in comparison to the commercial tools (ASTAR)[42], b) 3D-crystal orientation mapping of a nanocrystalline perlitic steel tip [103], c) Lorentz 4D-STEM of the local magnetic domain structure in a dual-phase ferromagnetic Fe-Co-Ge-Ti alloy [29], d) In situ liquid cell 4D-STEM under electrochemical conditions in a 400 nm thick liquid layer, e) Charge density mapping (colour image) to locate B/C (arrows) in a [001] tilt grain boundary in Fe [27], d) Multislice electron ptychography reconstruction of NaNbO<sub>3</sub> to determine 0 octahedral tilting

# 4D-STEM

Recent advancements in pixelated, direct electron detectors have enabled novel imaging and quantitative analysis strategies, where 2D diffraction patterns are collected for every probe scan position, termed 4D-STEM. With this, a dataset consists of thousands or even millions of diffraction patterns and manual data analysis becomes nearly impossible.

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We have developed a Python-based open-source toolbox within pyxem to perform automated crystal orientation mapping using a pixelated detector (see Fig. 2a) [42]. Such techniques were previously only available through commercial hard- and software and it is shown that by using the parallelizability of the code, it is even possible to enable data analysis at comparable time scales than the data acquisition. These developments have been setting the stage to combine automated crystal orientation mapping with tomographic tilt series to obtain the 3D crystallographic information of nanomaterials [103] as shown in Fig. 2b. In an ongoing effort, we are now correlating the 3D crystal orientation mapping and atom probe tomography (APT) on the same specimen to resolve both structural grain boundary parameters and composition at highest spatial and chemical resolution in 3D.

Recently, we have established Lorentz STEM techniques to determine the local magnetic induction in magnetic specimens using segmented and pixelated detectors [29]. Since the local magnetization is proportional to the magnitude of the beam deflection, it is even possible to determine quantitative magnetization values with nanometre resolution. We found that vortex-like magnetic domain states emerge in disordered body-centred cubic A2 Fe-Co phases in a dual-phase Fe-Co-Ti-Ge alloy as shown in Fig. 2c.

By using an aberration-corrected probe at semi-convergence angles typically larger than 17 mrad, it is possible to determine local electric fields and reconstruct phase images essentially realizing linear imaging conditions. This is beneficial to resolve light elements at atomic resolution and we have shown that such 4D-STEM measurements can provide unique insights into the location of B and C in Fe tilt grain boundaries (see Fig. 2e) [27]. This information was so far only attainable from computer simulations and it is now possible to establish better models to determine the intrinsic effects interstitial solutes have on interface properties.

### Grain boundary segregation transitions

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The influence of alloying elements and impurity atoms on grain boundary properties is ubiquitous across different material systems, but a fundamental role how such elements impact interfacial properties is often missing. We used Fe-4at.%Al bicrystals to explore how interstitial solutes affect grain boundary composition and structure. We found that the segregation of both B and C to a  $\Sigma 5$ (310) [001] tilt grain boundary induces a depletion of Al, which is related to repulsive interaction between B/C and Al [51]. Correlated density functional theory calculations in collaboration with D. Schreiber and L. Romaner (Materials Center Leoben) show that B and C exhibit a strong segregation tendency due to their preferred binding in the interstitial volume of the kite-type grain boundary structure. Based on these results, we systematically investigated the effect of grain boundary structure and composition on liquid metal embrittlement (LME) of Fe with Zn. LME is a complex process, which leads to catastrophic material failure and with this, tremendous economic losses, but the underlying atomistic mechanism is not fully understood. We observed that Zn forms a complex nanoscale segregation pattern ahead of the liquid penetration layer, which is related to a phase decomposition in collaboration with R. Kamachali (Bundesanstalt für Materialforschung und -prüfung, BAM) at the interface [37]. Furthermore, it is found that B and C have the propensity to partly repel Zn from the grain boundary and offset its detrimental effects on interface cohesion.

In recent work, we found novel segregation transitions induced by Fe in tilt grain boundaries in Ti. Atomic resolution imaging and spectroscopy reveals that icosahedral cage-like structures are forming at the interfaces upon Fe segregation [108]. These cages can even assemble to cage-clusters and are observed at symmetric and asymmetric grain boundaries (Fig. 3). By combining our atomic resolution observations with novel grain boundary structure prediction in collaboration with T. Frolov (Lawrence Livermore National Laboratory) it is found that the cage structures are robust building blocks of different grain boundary phases and that they can accommodate much higher levels of Fe than the pristine Ti grain boundary.



**Fig. 3:** Observation of novel icosahedral grain boundary states in symmetric and asymmetric [0001] tilt grain boundaries in Ti. a) shows isolated icosahedral cages in an asymmetric grain boundary. In b) and c) the formation of icosahedral cage clusters is found in both an asymmetric (b)) and symmetric (c)) grain boundary.

## **Compositionally complex materials**

Compositionally complex materials have evolved into a material class that is spanning from structural alloys to functional catalysts as well as oxides and even 2D materials. The vast composition and phase spaces allows to establish materials with novel properties and we have systematically investigated the deformation behaviour in refractory high entropy alloys with body-centre cubic structure [43]. It is found that the formation of kink bands plays a pivotal role in the deformation mechanism, which is distinct to that from high entropy alloys with facecentred cubic structure. Usually, the formation of brittle topologically complex intermetallic phases is regarded to be detrimental for the mechanical properties of alloys, but we could show that in a metastable Fe<sub>34</sub> Mn<sub>20</sub>Co<sub>20</sub>Cr<sub>20</sub>Ni<sub>6</sub> (at.%) alloy, both strength and ductility can be enhanced since the displacive phase transformation during deformation around the intermetallic precipitates prevents the initiation of crack formation and hence early material failure [35]. Such multiphase compositionally complex alloys are also interesting material candidates for high temperature applications in harsh environments and we have explored the intrinsic phase transformation pathways in the Fe-Cr-Ni-Co [65] and light-weight alloys in the Fe-Cr-Ni-Al-Ti system [109]. For the first system, additive manufacturing was successfully used to print 99.9 % dense nano-dispersion strengthened alloys with superior powder processing conditions [95,110] and improved final mechanical properties [65] of the printed structure compared to the pure Fe-Cr-Ni-Co matrix (cooperation within SPP 2006 CCA-HEA, see p. 89). The above mentioned Fe-Cr-Ni-Al-Ti alloys [109] are composed of disordered body-centred cubic A2 and L21-ordered Heusler phases and we have taken this general phase-arrangement concept to establish novel soft-ferromagnetic alloys in the Fe-Co-Ti-Ge system with high Curie temperature [29,34]. We could show that by compositional tuning it is possible to establish different phase arrangement of the bcc-A2 and L2,-phases, which directly impacts the bulk magnetic properties. By in situ Lorentz TEM imaging it was possible to demonstrate that there is a strong interaction of magnetic domains between the two phases, which plays an important contribution to the coercivity of these materials.

# Atomistic Modelling of Material Interfaces (T. Brink)

#### Group mission

The aim of the group is to understand structure-thermodynamics-property relations of interfaces, in particular grain boundaries (GBs). We use atomistic computer simulations for modelling the atomic-level interface structures in close collaboration with STEM imaging and micro-/ nanomechanical testing experiments in the department. In this context, the simulations enable deeper insights into 3D structure, thermodynamics, and plasticity mechanisms, which are often experimentally inaccessible at the atomistic length scale.

#### Structural variety of grain boundaries in pure fcc metals

We started investigating symmetric [111] tilt GBs as an interesting example case in collaboration with the *Advanced Transmission Electron Microscopy* group. Molecular dynamics (MD) simulations predict that these GBs exhibit two different atomic structures ("pearl" and "domino") on the same GB plane (Fig. 4). In Cu, both motifs were also found with STEM experiments [40], while only domino was found in Al [32]. In terms of interface

thermodynamics, domino and pearl are GB phases (also called "complexions"), meaning that they can undergo GB phase transitions based, e.g., on temperature or applied stress. We used molecular statics and MD simulations on different [111] tilt GBs over a range of fcc metals to explore if the GB phases that occur are indeed material specific. This is not the case: all investigated fcc metals and even simulations with model pair potentials universally exhibit both the domino and pearl phases, which are thus a result of the densely-packed fcc host structure [71]. The thermodynamic stability of the GB phases, however, is strongly specific to the material. Indeed, the pearl phases in AI are predicted by the computer model to be stable only at higher temperatures or not at all (depending on the specific GB parameters), explaining why no pearl phase was found experimentally [71]. This work furthermore underlines that GB phase transitions are likely a common phenomenon and not specific to a material.



**Fig. 4:** GB phases in [111] tilt boundaries of fcc metals. (a) The domino phase (middle) is in fact a nanofaceted boundary, consisting of two "zipper" facets. (b) On the same plane as the domino phase, a pearl GB phase can also be observed. (c) The pearl and domino GB phases can be detected using machine-learning tools developed in a collaboration with ICAMS. Here, the colouring of a sample with both GB phases was automatically applied. Image courtesy of Mehrdad Madavi Jafari (ICAMS, RUB).

The pearl and domino phases in Fig. 4 (c) were coloured automatically by an algorithm for GB phase classification using machine-learning techniques that we are currently developing in cooperation with M. Stricker (ICAMS, RUB).

In addition to the symmetric GB plane, which exhibits domino and pearl, there is another GB plane, inclined by 30°, which exhibits a structure we call the zipper phase [32,36,38] (Fig. 4 (a), left and right). Closer inspection of the domino phase shows that it consists of similar structural units as the zipper phase (Fig. 4 (a)), suggesting that it is simply a faceted GB. However, the line defect connecting the facets (facet junction) usually has a Burgers vector [32] and consequently contributes a defect energy and thus a driving force for facet growth. The facet



lengths of the domino phase are on the order of 1 nm and very regular. Using computer simulations, we could however show that the facet junctions of the domino phase lack a Burgers vector and have instead an attractive interaction due to alternating GB excess stresses of the facets [30]. This is thus the first description and observation of energetically stable nanofacets. It is yet unclear if this phenomenon is exotic, given that atomic resolution imaging is required to observe the nanofacets and data in literature is rare.

### Shear-coupled motion of grain boundaries

These results pose the question if such structural differences between GB phases affect any properties. It is known that GBs migrate under applied shear stress, coupling the shearing of two abutting crystallites to the GB's normal movement. In the case of domino and pearl, interesting effects occur: For a  $\Sigma$ 7 GB, these two GB phases indeed move in opposite directions, while for a  $\Sigma$ 19b GB they move in the same direction under the same applied



**Fig. 5:** Segregation of Ag to tilt boundaries in Cu. The graph shows the excess Ag concentration as a function of the chemical potential difference obtained with hybrid MD/Monte Carlo simulations. The snapshots (a)–(d) correspond to the indicated data points. We can see that the structure of the GB does not change, but that excess concentration jumps are correlated with a change of segregation patterns (GB phase transition). Simulations by Dongjin Kim. stress and boundary conditions [72]. This intricate dependence of GB migration behaviour is determined by the possible disconnections, which are dislocation-like defects on GBs. A detailed analysis of the GB and disconnection structure revealed that the active disconnection mode (and thus the GB propagation direction) depends on the structural motifs of the GB at an atomic level and thus on the GB phase [72]. An investigation of asymmetric GBs is under way in order to generalize these results to more realistic, imperfect GBs.

## Grain boundary segregation

While the modification of interface behaviour based on GB phases is potentially useful ("defect engineering"), it is not feasible to easily control the GB phases in pure materials: The temperature and stress conditions are likely constrained by the application and cannot be used to change the GB phase. Similar to the bulk case, alloying is a good strategy to control the GB phase via the excess concentration (see also p. 214). We were able to correlate the segregation of Ag to a  $\Sigma$ 37c zipper structure between experiment and simulation [36]. Currently, no usable measurements on segregation to domino and pearl exist, but simulations suggest that there are significant differences in the excess concentration and in the GB phase transitions as a function of chemical potential (Fig. 5).

A more striking interplay between segregation and GB phases could be found in experiments on Ti–Fe [108], where a new icosahedral structure appears when Fe segregates to the GB. Our hybrid MD/Monte Carlo simulations show that there are GB phase transitions between different levels of segregation, which however do not correspond to layering transitions, but to the formation and agglomeration of cage units.

A related property to GB segregation is GB diffusion. In a collaboration with (among others) the University of Münster and ICAMS, we investigated diffusion in Ni  $\Sigma$ 11 GBs. The Cr-diffusion in a sample with this GB shows two contributions. Using simulations, we found that this does not correspond to GB phase transitions, but to differences between GB diffusion and diffusion along line defects of the GB [111].

#### Mechanics

In collaboration with the *Mechanics at Chemical Interfaces* group, we are studying how segregation affects the transmission of dislocations through the GB. In the classical Hall–Petch picture, GBs are simply obstacles. Experimental results [13], however, show that Ag segregation to a  $\Sigma 5$  GB in Cu increases the yield strength of a micropillar. With MD simulations we found that Ag pins the dislocation while pure Cu GBs absorb the dislocation (Fig. 6). We are currently working on connecting these observations to the observed hardening effect.

As a first step towards bringing experiments and MD simulations of plasticity closer together across the disparate time scales, we collaborated with the *Extreme Nanome*- chanics group. We explored the deformation of pristine, defect-free Ni nanoparticles under high strain rate compression [112]. Using MD, we found that there is a size effect on the particle yield point due to pinning of the initial dislocation loop at features that scale with the particle size. Taking the size effects into account, simulation and high strain rate experiments agree in the trends for the yield strength [112]. In the future, this work will be extended to samples with GBs and other defects.



**Fig. 6:** Dislocation transmission through  $\Sigma$ 5 GBs in Cu. (a) MD simulation of compression of a sample with periodic boundary conditions, which initially contained a dislocation network. The left sample is pure Cu and shows a depletion of dislocations during deformation, while the right sample exhibits Ag segregation to the GBs and no dislocation depletion. Detailed simulations of dislocation transmission show that pure Cu GBs (b) absorb the dislocation, which splits off into disconnections, while GBs with Ag segregation (c) do not allow the splitting into disconnections and instead lead to a pile-up.

# Mechanics at Chemical Interfaces (J.P. Best)

### Group mission

The mission of the group Mechanics at Chemical Interfaces is to link the local structure and chemistry of defects, such as grain boundaries, with their mechanical deformation responses at nano- and microscales. We achieve this using nanoindentation devices within scanning electron microscopes (SEMs), typically on microscale specimens prepared using focused ion beams. Our group is committed developing advanced testing infrastructure, such as for the mechanical testing of solid-state batteries, and creating correlative workflows with atom probe tomography (APT) analysis of deformed materials. By addressing key questions in energy and nanostructured materials, and interfacial mechanics, the group aims to develop sustainable materials solutions to meet society's evolving needs. Our research is organised into three main themes: Fracture at Interfaces, Interfaces in Energy Materials, and Nano- and Microscale Plasticity.

## Nano- and Microscale Plasticity

Regarding nano- and microscale plasticity, our group examines size effects on plastic deformation [113], utilising in situ micropillar compression coupled with nanoindentation [10], often complemented by APT and TEM analyses, to link local structural and chemical parameters. Recent, and as yet unpublished, work has focused on single crystals of iron oxides and iron aluminides, understanding fundamental plasticity phenomena at nanometre and micron length-scales, including at elevated temperatures. We are also keenly interested in the role of grain boundaries on the local mechanical response using micropillar compression, whereby dislocation-GB interactions can be studied in detail, as demonstrated for our recent work on twin boundaries in Cu bicrystals [11,15]. By varying the chemical decoration of GBs and studying its effects on plasticity, we have investigated copper high-angle grain boundaries containing silver [13]. Using Cu-Ag as a model system, we compared the mechanical response of pure Cu bicrystals to Ag-segregated Cu bicrystals. This system is common in electronic components to prevent electromigration, and since Ag is almost immiscible in the Cu matrix, it preferentially segregates to GBs, allowing us to isolate the effect of the GB chemistry on the mechanical response. We found significant effects of Ag segregation on GB strengthening, which could then be coupled to atomistic simulations of T. Brink to better understand the underlying mechanisms, where Ag pinned incoming dislocations to the GB plane, providing valuable insights into our observations.

## Fracture at Interfaces

The Mechanics at Chemical Interfaces group focuses on the fracture properties of materials at microstructural length-scales, particularly at grain and phase boundaries. Using *in situ* small-scale testing methods within the SEM, we can probe site-specific fracture properties and

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gain insights into material failure mechanisms, as has been recently demonstrated for C15 CaAl, Laves phases as part of SFB 1394 (see p. 82) [5,114]. Our collaboration with FZ Jülich and E. Bitzek (CM) has led to detailed studies on the embrittlement of recrystallised tungsten due to phosphorus segregation at grain boundaries (GBs) [6]. This study linked experimental microcantilever tests using sharp notches located at individual grain boundaries, to local information from APT and atomistic simulations. There it was found that an enrichment of 2 at.% phosphorous at the high-angle GBs led to reduced plastic dissipation and corresponding embrittlement (see Fig. 7). Such insights and approaches are novel in the community, and will allow for further advanced analyses of mechanics at complex interfaces. As such, we have begun exploring other materials systems, such as the high-temperature oxidation of Fe-Cr alloys. Using novel in situ approaches to study local fracture at grain boundaries and understand the impact of oxygen accumulation at GBs on material integrity [114], we have observed that GB-oxides are important damage nucleation sites affecting the global mechanical properties of the alloy.



**Fig. 7:** Fracture at high-angle GBs in recrystallised tungsten. In situ testing of microcantilever of 2  $\mu$ m width × 2  $\mu$ m breadth and corresponding electron backscatter diffraction image of cantilever (a). Magnified image of sharp notch located at GB plane (b). Post-mortem image of the cantilever cross-section shows brittle fracture (c), which is supported by molecular dynamics (MD) simulations (d), and linked to a chemical enhancement of phosphorous by APT (e).

### Interfaces in Energy Materials

Interfaces in energy materials are critical for the performance and reliability of devices such as batteries, fuel

cells, and solar cells. Our research investigates the mechanical behaviour at these interfaces, crucial for the structural stability and durability of materials under various conditions, as recently demonstrated for our nanoindentation study of δ-phase boundaries in Ni-based superalloys, where adjacent  $\gamma^{\prime\prime}\mbox{-}free$  zones characterised by APT showed higher deformability [115]. Our study of defects in electrode materials, particularly iron oxides for water electrolysis, focuses on how microstructural defects can enhance the catalytic performance of electrodes during the oxygen evolution reaction, where we have already performed systematic studies on iron oxide formation using magnetron sputtering [4]. Supported by the IMPRS SusMet doctoral school (see p. 80) and in collaboration with K. Tschulik (RUB), this work is providing valuable insights into the role of defects in electrochemical performance. Our partnership with J. Rupp's group at TU Munich further aims to address the chemo-mechanical compatibility issues in solid-state lithium-ion batteries, improving the interface between active materials and solid electrolytes.

Our research on nanostructured thin-films for electronics focuses on how local chemistry and structure affect the mechanical and electrical performance of advanced coatings [12,14], including thin-film metallic glasses (TFMGs) [16,21], deposited using magnetron sputtering. Collaborative efforts with institutions like Sorbonne Paris Nord, supported by the German Academic Exchange Service (DAAD) and French National Centre for Scientific Research (CRNS) Salto programmes, allow us to explore the effects of nanostructuring on both crystalline and amorphous metallic thin-films. We investigated the activation of mechanical size effects in TFMGs, showing that introducing interfaces within the glass structure can enhance mechanical properties by hindering shear band propagation [19,116]. This research is crucial for developing high-performance electronic devices and understanding the fundamental mechanisms governing their behaviour.

### **Future Directions**

Looking ahead, the research of the group will continue to focus on the fracture and plasticity at interfaces, and link to chemical variation. Key themes will be, for example, the mechanical testing of solid-state batteries and the development of robust testing infrastructure to address the critical challenges associated with the chemo-mechanical stability of solid-state lithium ion batteries (see Fig. 8 and p. 62), furthering our in situ SEM nanomechanics of water ice [117] (see p. 220), or investigations into recycled alloy materials where impurity effects are critical. Such efforts for batteries will ensure their reliability and performance for next-generation energy storage solutions. For chemically-complex recycled metallic alloys, mechanistic insights can be delivered on the role of impurities on failure at GBs and how these effects can be ameliorated.



**Fig. 8:** Preliminary results on solid-state lithium ion battery (LiB) testing. Custom cell for battery cycling (a) is used to test damage of the solid-state LLZO electrolyte, where an auto-slice SEM image of the pristine electrolyte is shown (b) taken at cryogenic conditions to suppress e-beam induced degradation. Resulting cycling (c) and impedance spectroscopy (d) results showing LiB performance over time.

# Nanomechanical Instrumentation and Extreme Nanomechanics (XNano) (R. Ramachandramoorthy)

### **Group Mission**

The XNano group was formed in August 2020, with a focused goal of pushing the horizons of micro/nanomechanical testing and microfabrication beyond the state-of-the-art. Small-scale mechanical characterization is essential to extract vital microstructure-property relationships from nano-to-meso scale materials. Yet, the small-scale testing research is primarily limited to quasi-static and ambient temperatures owing to severe hardware and protocol limitations. As such, pushing micro/nano mechanical characterization via nanoindentation and compression/tension to extreme conditions of strain rates and temperatures constitutes the first core mission of the group. In terms of small scale fabrication, the group's second core mission is to develop micromanufacturing methods, beyond traditional UV-lithography and FIB based erosion [2], which will enable high throughput and true freeform 3D/4D printing of metals with micro and nanoscale resolution.

### **Extreme Micro/Nanomechanics**

Metallic alloys and ceramics are integral to numerous engineering applications due to their exceptional mechanical strength and durability. Traditionally, the mechanical behaviour of these materials under quasi-static conditions has been the focus for the design and development of components across various demanding fields. However, real-world scenarios often subject these materials to rapid mechanical stimuli, resulting in strain rates ranging from  $10^3$  to  $10^7$  s<sup>-1</sup> over mere microseconds. This abrupt increase in energy demands an in-depth investigation of the dynamic strength and failure mechanisms of materials at multiple length scales from macro-to-nano: given the well-established material size effects [1]. Specifically, at the micro-to-nano scales, mechanical metrology using nanoindentation and micro/nano compression/tension is carried out at strain rates <0.1 s<sup>-1</sup> – owing to the hardware limitation of the small-scale *in situ* testing platforms and the lack of precise methodology and protocols for dynamic testing [118,119].

Addressing this research gap, a high-speed piezo-based micromechanical experimental setup was engineered to achieve constant indentation strain rates of  $10^5$  s<sup>-1</sup> (Fig. 9a) and micro/nano compression strain rates beyond  $10^3$  s<sup>-1</sup> [120]. Specifically, the different essential components of any mechanical testing system such as actuators, load sensors, displacement sensors and the acquisition systems, along with the necessary support electronics hardware and post-processing protocols were optimized for successfully obtaining load-displacement (or stress-strain) signatures from such small-scale dynamic tests. Optimal piezotube actuators with low capacitances (<10 nF) and high-speed high-voltage high-current amplifiers were chosen to enable high speed movements up to 100 mm/s.



**Fig. 9:** a) Ultrahigh strain rate-dependent indentation response of nanocrystalline nickel. b) Constancy of indentation strain rates can be achieved even upto  $10^{5} \, \text{s}^{-1}$ .

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High stiffness load sensors that do not resonate during high speed testing were designed for different load ranges: <10°mN and <1 N, based on piezoresistive (see p. 85) and piezoelectric methodologies respectively. Displacement sensors with nanometre precision based on piezoresistive strain gages, along with the necessary strain gage amplifiers with a high bandwidth of ~2°MHz were calibrated using a laser interferometre and used for the dynamic testing. The load and displacement signals were captured using oscilloscopes with sampling rates up to 10° counts/s. Finally, several post-processing protocols including signal synchronization with microsecond precision, time constant correction to account for electronics-based lag and inertial corrections based on mechanical modelling were implemented.

This highly custom-modified micro-/nano-mechanical testing platform enabled constant high strain rate compressions of micropillars, microlattices, microparticles, nanowires (see p. 71) and nanoparticles at strain rates up to  $10^3 \text{ s}^{-1}$ . Further, constant strain rate indentations up to  $10^5 \text{ s}^{-1}$ , for the first time, have been successfully conducted in a variety of material systems including nanocrystalline nickel (Fig. 9b), fused silica, copper, iron-aluminide intermetallic and molybdenum [122].

# Additive Micro/Nanofabrication

Two different manufacturing methodologies were chosen to accomplish the goal of high throughput and 3D/4D metal printing of small-scale samples. Specifically, thin film based solid-state dewetting was explored as a high throughput technique to fabricate pristine self-similar single-crystalline micro/nanoscale metal and alloy particles. 3D/4D printing of metals/alloys was approached using a nascent yet promising additive micromanufacturing technique of localized electrodeposition in liquid (LEL), part of the research funded via the recently obtained ERC Starting Grant AMMicro (see p. 57).

a) Thin film dewetting: Micro/nanoparticle fabrication

B2 intermetallic microparticles are strain rate insensitive (Fig. 10a).

b) Localized electrodeposition in liquid

LEL technique utilizes localized electrodeposition via a hollow-AFM (atomic force microscopy) cantilever to deliver metal ions, which get reduced in the working electrode (conductive substrate) to form micron scale metal droplets - while being submersed in a supporting conductive electrolyte solution. Using a precise positioning of the cantilever to different coordinates, voxel-by-voxel layer-by-layer 3D microarchitectures can be fabricated. Using this technique, a variety of metallic architectures, primarily of highly twinned ultrafine grained copper, including micropillars [123], microlattices [124], liquid-filled and sealed metal microcylinders etc., have been successfully realized, Fig. 10b. Subsequently, unique microstructure-architecture-rate/temperature dependent mechanical property relationships have been established for several copper microarchitectures. Specifically, the rate- and temperature dependent mechanical properties of liquid-filled copper microcylinders involving unique liquid-to-ice and liquid-to-vapour phase transitions have been identified (see p. 220).

Further, the rate-dependent energy absorption properties of copper octet [124] and honeycomb microlattices have



**Fig. 10:** a) The yield stress of dewetted iron-aluminide B2 intermetallic particles with different diametre ranges (Ø) compressed at strain rates between 0.01/s and 1000/s. b) 3D microscale metal architectures: micropillar, octet microlattice and push-to-pull microcylinder manufactured using the LEL printing technique. also been established, as a means of evaluating their suitability as efficient and cost-effective localized impact protectors for sensitive MEMS/NEMS systems. Recently, through the DFG-funded weave lead agency project MIMIC, we plan to characterize the highly impact resistant skulls of musk-ox for their responsible ultrastructural motifs and using the lessons learned, design novel metamaterials with superior energy absorption/impact mitigation properties.

# Hydrogen Mechanics and Interfaces (M.J. Duarte Correa)

# Group mission

The broad mission of the group is understanding the role of environmental factors, particularly hydrogen, on the mechanical behaviour of materials. Different aspects of the material microstructure, external conditions and mechanical loading are considered to scrutinize the interactions of materials with hydrogen (Fig. 11a). We aim to provide guidelines for materials used in a hydrogen supported economy and prevent hydrogen-related material's failure. The group was established in 09/2019 supported by third party funding and became permanent in 04/2024.

With the increasing need of using hydrogen as energy carrier to reduce  $CO_2$  emissions, it became evident that a proper assessment of the materials used is pressing. Moreover, hydrogen affects as well other materials where hydrogen is introduced from environmental factors, such as in large infrastructure like bridges and boats. Here, the

use of hydrogen-resistant materials assists to increase safety and sustainability by reducing maintenance. The macroscopic material's failure associated with hydrogen is called hydrogen embrittlement, and it is a complex process that originates at the atomic scale by the diffusion of hydrogen into the material and its accumulation at specific sites. Understanding how hydrogen affects a material or which embrittlement mechanism is dominant, requires to study individual hydrogen-microstructure interactions, thereby targeting analyses at the nano-/microscale during hydrogen exposure. To reach our goal, we develop new instrumentation to perform micromechanical testing during hydrogen charging, while targeting individual material features, and we correlate the mechanical findings with high-resolution and state-of-the-art microstructural and hydrogen characterization.

## Instrumentation development

We develop in-house unique instrumentation to allow different environments during mechanical testing and particularly control the ingress of hydrogen into the studied materials. The "back-side" (Fig. 11b) and the "front-side" (Fig. 11c) hydrogen charging setups consist on 3-electrode electrochemical cells with the sample acting as working electrode, where the hydrogen evolution reaction takes place [28]. The hydrogen produced in this way at the sample surface, further diffuses into the bulk of the material as shown in the schematics. These cells are mounted into a standalone nanoindenter that allows conducting different types of mechanical testing during hydrogen supply, such as nanoindentation, nanoscratching, pillar compression and more. A main advantage of the backside approach is that the tested surface is never in con-



**Fig. 11:** Schematic representations of a) hydrogen-microstructure interactions, b) back-side and c) front-side setups for in situ hydrogen (H) charging during nanoindentation (the upper sections show the entry and diffusion of hydrogen into the material). Examples conducted on a Fe-20 wt.% Cr alloy: d) cross-section bright-field STEM image of dislocations beneath a nanoindentation imprint performed during hydrogen charging of a single (1 1 0) grain; e) micropillars compressed without and during hydrogen charging in a single (1 0 0) grain; f) cross-section bright-field STEM image of a nanoindentation imprint performed during hydrogen charging of a nancocrystalline sample.

tact with the electrolyte, preventing in this way unwanted corrosion and surface damage, as it could happen for the front-side strategy. Since hydrogen requires to diffuse through the sample thickness, diffusive processes can be as well studied in time dependent measurements and then correlated to other techniques such as Kelvin probe. One added advantage of the back-side charging is the possibility to fully transfer the cell into other systems for a more complete understanding of hydrogen interactions. For example, we successfully fitted our back-side setup into a synchrotron facility to create maps of the lattice strain during pillar compression and hydrogen charging. Currently, we are as well introducing a similar design for nanoindentation inside an environmental SEM.

#### Plastic deformation and diffusive hydrogen

A critical challenge in the study of hydrogen-induced damage is the understanding of failure initiation and the significant role played by mobile hydrogen at service conditions, since it can diffuse and accumulate at stress-concentrated regions. Current studies on hydrogen effects are in their majority limited to post-mortem probes and *ex situ* charging, which neglect diffusible hydrogen and its migration and desorption at the analysis time, and a large amount of mobile hydrogen can be lost. Here is where the back-side charging approach stands out and allows differentiating between the effects of trapped and mobile hydrogen levels monitored over time and consider hydrogen absorption, diffusion and release through the metal.

Dedicated nanoindentation experiments on Fe-X model alloys, with X=Cr, Al, Ni, are performed as a function of time while varying the level of hydrogen introduced into the material. The energy necessary to nucleate dislocations is reduced, while the hardness is increased for higher content of hydrogen and substitutional elements, which act as flat trapping sites for hydrogen. The relationship of hardness increase as a function of the hydrogen supply can be seen in Fig. 12. The changes in the dislocation structure and the increase in dislocation density are further studied by TEM (Fig. 11d). These results together with analyses by micropillar compression (Fig. 11e) imply an increment in the dislocations interactions and pinning on the dislocation motion connected to hydrogen [69]. Interestingly, the changes in the mechanical behaviour induced by hydrogen can be used also as indicators of the hydrogen diffusivity through the metal in the backside charging configuration (see p. 204).

## Role of interfaces on decohesion and cracking

Interfaces, such as grain and phase boundaries, are known to be largely responsible of a material strength, but they also represent important sites for damage nucleation. In relation to hydrogen, interfaces can act as trapping sites, causing embrittlement and material failure. The density of interfaces, their character and energy, and possible solute segregation are key factors to under-

stand the hydrogen trapping behaviour, further damage and possible interface decohesion and cracking. The study of interfaces is carried out in commercial alloys, such as in ferritic and austenitic steels (see p. 103), as well as martensite-ferrite dual phase steels. In terms of model alloys, one way to increase the density of grain boundaries of our well researched Fe-20 wt.% Cr alloy, is to perform high-pressure torsion followed by annealing, to reach the desired grain size (Fig. 11f). Initial nanoindentation studies without and during hydrogen charging show the effect of hydrogen on hardness and dislocation behaviour. For the nanocrystalline FeCr alloy, a two-step protocol allows to suggest that hydrogen trapped at the grain boundaries boosts the hardening effect observed in the single grain approach. The study of the trapping behaviour is currently carried out in collaboration with M. Rohwerder (GO) by Kelvin probe and B. Gault (MA) by atom probe analyses, as well as external collaborations by secondary ion mass spectrometry.



**Fig. 12**: Relative hardness change due to hydrogen ingress into Fe-X alloys (X=Cr, Al). A higher current density indicates a higher hydrogen supply.

#### Hydrogen barrier coatings

Hydrogen barrier coatings represent an appealing option to prevent or slow down the hydrogen ingress into structural materials that are susceptible to hydrogen embrittlement [77]. We study these systems in collaboration with the group Nanoanalytics and Interfaces (C. Scheu). The microstructural characterization is correlated with the hydrogen diffusion and trapping [75]. Moreover, the mechanical behaviour is analysed at small-scale by nanoindentation and nanoscratching without and during hydrogen charging to understand changes in the mechanical behaviour of the coating and the substrate independently, but focussing on the interface performance and possible delamination [76], see p. 92.

# Intermetallic Materials (M. Palm [until 05/2023], and F. Stein)

# Group mission

The work of the group Intermetallic Materials focuses on fundamental aspects of the thermodynamic stability, structure, and transformations of intermetallic phases. Besides the goal of gaining an improved fundamental understanding of such phases, this also involves the design of novel sustainable materials based on intermetallic phases for possible use in structural applications. A key prerequisite for any new material development is a sound understanding of the stability of the constituent phases and their thermodynamic equilibria as a function of composition, temperature and time, which is why the investigation of phase diagrams is an important part of the group's work. Activities in the reporting period have focused on Fe-AI- and Ti-AI-based intermetallic alloys and on Laves phases and related structures.

### Iron aluminides

Fe-Al alloys in the composition range of about 25 to 50 at.% Al are low-cost, sustainable materials with outstanding corrosion resistance and comparably low density. Their potential to replace Cr-Ni-steels or Ni-base superalloys in turbine parts for applications up to 700 °C has been evaluated in the large-scale collaborative project "Pro-FeAI". High creep strength is a prerequisite for such applications. Respective measures for improving the creep strength at these temperatures in Fe-Al alloys have been investigated in our group [82.84.86]. One of the most effective ways is strengthening by fine-scaled Laves phase precipitates. However, such a fine-scaled distribution can only be obtained when the nucleation of the Laves phase is preceded by formation of a metastable Heusler phase. For a detailed understanding of this transformation, phase equilibria in the Fe-Al-Nb system were investigated by combined SEM, X-ray diffraction (XRD) at room temperature and up to 930 °C, electron probe microanalysis (EPMA), and differential thermal analysis (DTA) with emphasis on determining the range where the Heusler phase and Laves phase form [84,86]. In collaboration with the MA department, the kinetics of the transformation from the metastable Heusler phase to the stable Laves phase were studied by APT [82]. At a given temperature, the transformation in the Nb containing allovs proceeds much faster than in those alloved with Ta. Apart from the fact that Nb diffuses faster than Ta. the surprisingly much lower Nb content in the Heusler phase is the reason for the faster transformation [82,86]. Based on these results, the industrial partners were able to manufacture forged turbine blades whose yield strength and creep resistance matched those of the laboratory samples [125].

While the Heusler phase is metastable in Ta- or Nb-containing alloys, stable coherent microstructures of a disordered ferritic matrix and intermetallic Heusler precipitates can be obtained by adding Ni and Ti to Fe-Al. In collaboration with the group Advanced Transmission Electron Microscopy (C. Liebscher) and the Department of Material Science, Montanuniversität Leoben, Austria, the formation and thermal stability of such microstructures in Fe-20Al-10Ni-10Ti (in at.%) was studied by combined SEM, TEM, HT-XRD, DTA, and APT investigations. Though coherent microstructures resembling the  $\gamma/\gamma'$ microstructure of Ni-based superalloys formed, the Heusler precipitates with an initial size of < 100 nm coarsened rapidly at 900 °C [126].



**Fig. 13:** Concentration profile (top), nanohardness (middle), and indentation modulus (bottom) along the concentration gradient of a single-phase B2 FeAI diffusion couple. The background colours indicate the orientations of the different grains. The middle diagram shows the already known, but yet unexplained sudden hardness increase at a composition of about 39 at.% AI with no visible effect of the grain orientation. In contrast to that, the indentation modulus clearly shows a dependence on orientation, which is in accordance with the expected behaviour for cubic crystals (lowest modulus in 001 direction).

In the entire composition range between about 30 and 50 at.% AI, Fe-AI alloys are cubic *B2*-ordered single-phase materials with disordering temperatures of at least 1000 °C. Interestingly, the mechanical behaviour as a function of the AI content varies in a very particular way within this extended composition range. When increasing

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the Al content to >40 at.%. an unusual, abrupt change in e.g. yield strength and hardness is observed and the brittle-to-ductile transition temperature strongly increases, while the B2-ordered structure remains unaffected. To unravel this surprising effect, which is still not well understood, we have chosen a novel experimental approach that allows for a much more systematic investigation of this phenomenon than previously reported in the literature. By preparing diffusion couples of an Al-poor and an Al-rich alloy (e.g., with 30 and with 50 at.% Al), extended concentration profiles of several mm in length are produced covering the entire composition range. Micromechanical testing methods such as nanoindentation and micropillar compression, which are carried out in collaboration with the Mechanics at Chemical Interfaces group, then enable the systematic investigation of mechanical properties as a function of composition and temperature over the entire homogeneity range of this phase in only one sample under conditions that are identical for all compositions. Some preliminary results of this ongoing project showing the above-mentioned sudden increase in hardness are presented in Fig. 13.

At Al contents exceeding 50 at.%, the cubic,  $\gamma$ -brass type phase Fe<sub>5</sub>Al<sub>8</sub> occurs in the Fe-Al system as a high-temperature phase stable in a small temperature interval between 1095 and 1231 °C. It decomposes in a very rapid solid-state reaction, and the very rare phenomenon of dendritic solid-state precipitation of a phase (in this case B2 FeAl) can be observed here. In a collaboration with Guangxi University, Nanning, the formation and growth of these solid state dendrites could be observed *in situ* by applying confocal scanning laser microscopy [127].

## TiAl-based alloys

TiAl-based alloys have proven to be capable to replace Nibased superalloys at temperatures up to about 800 °C in applications such as, e.g., turbine blades in aero-engines. The effect of this 50 % decrease in weight is a significant reduction in fuel consumption and with that a decrease in greenhouse gas emissions. However, to achieve the ambitious goals of climate-neutral aviation set by the 'Advisory Council for Aviation Research and Innovation in Europe' (ACARE) of the European Commission for the year 2050 [128], the TiAl-based alloys currently in use and under development still need to be significantly improved, especially with regard to aspects such as their phase and microstructural stability at application temperature above 800 °C. As part of the EU-funded ADVANCE project (see p. 87), we have therefore performed systematic investigations into the complex phase relations in a series of ternary Ti-Al-X systems with X being the most relevant alloying additions Nb, Mo, W, Zr, Si, B, and O.

The most important alloying element, which also produces the most complex phase diagram, is Nb [87,88,129]. Above a critical content, Nb can stabilize the ternary intermetallic phases  $\omega_o$  and O, which significantly affect the material behaviour. By systematic DTA investigations combined with *in situ* high-energy XRD (HEXRD) (performed in collaboration with Helmholtz Zentrum Here-

on at DESY), both phases were found to decompose on heating in solid-state reactions in the temperature range between 900 and 1000 °C, which is of high relevance for the design of new Ti-Al-based alloys. For the first time, these decomposition reactions and the resulting phase equilibria were studied in detail, and it could be shown that the phase field of the particularly detrimental  $\omega_0$  phase splits into two parts above 800 °C due to the simultaneous formation of a small B2 ( $\beta$ Ti) phase field [87,129]. Comprehensive investigations were also performed on the phase equilibria in the systems Ti-Al-Mo [90,129], Ti-Al-Wi [89,129], Ti-Al-Si [93,130], Ti-Al-Zr [92,130], and Ti-Al-O [94,130].

## Laves phases

A long-standing topic of the Intermetallic Materials group is basic research on Laves phases, which are one of the most common intermetallic phases and occur in many applied materials. In a current project, which is a collaboration with the Advanced Transmission Electron Microscopy group, we aim at studying the structure of planar defects by high-resolution TEM in different types of off-stoichiometric transition metal Laves phase alloys. It is known from previous investigations that deviations from the ideal AB, Laves phase composition are mainly compensated by anti-site atoms, while a high density of planar faults can occur near the boundary of the composition range. In a preceding study on a NbFe<sub>2</sub> Laves phase alloy with a composition near the Nb-rich end of its homogeneity range, such extended planar defects were found to be stabilized by the excess Nb atoms forming structural motifs that are characteristic of the crystal structure of the neighbouring intermetallic phase in the system (which is a µ phase). In the chemically similar Cr-Nb system, which contains the Laves phase NbCr., no such u phase exists. First results from the current project indicate that in the case of Nb-rich NbCr, Laves phase, there is also a very high density of planar faults. However, in contrast to the case of NbFe, Nb-rich NbCr, does not contain comparable Nb-enriched structural motifs, but rather twins or stacking faults that do not allow the accommodation of excess Nb atoms. More detailed investigations of these defects are ongoing, and it is also planned to investigate the influence of such planar defects on the storage of hydrogen in the further course of the project.

Other projects in which the group was involved and which deal with Laves phases or structurally related phases, include topics such as the fracture behaviour of the cubic Laves phase CaAl<sub>2</sub> [5] (collaboration with the Mechanics of Chemical Interfaces group), the understanding of plasticity in Co-Nb  $\mu$  and Laves phases [131] (with RWTH Aachen University), the formation and particular compressive deformation behaviour of Nb<sub>2</sub>Co<sub>7</sub>, a monoclinic intermetallic phase with a crystal structure very strongly related to that of Laves phases [132-134] (with Hokkaido University of Science), and a re-investigation of the complex phase relations in the Cr-Ti system, where the three Laves polytypes C14- and C36-TiCr<sub>2</sub> (both with hexagonal structure) and C15-TiCr<sub>2</sub> (cubic structure) co-exist [135] (with Université Paris-Saclay).

The extensive experience and knowledge of the properties of Laves phases had motivated the publication of a comprehensive review article on Laves phases [136], which was awarded the "William Bonfield Prize for the best review paper" by the Journal of Materials Science in 2022 [137].



**Fig. 14:** The diagram in (a) shows an isothermal section through a ternary system with extended phase fields, where the coloured areas define the 'Alkemade regions'. Although the Alkemade theorem is not directly applicable in such cases, copying these regions onto the liquidus surface as shown in (b) allows some helpful conclusions about the position of maxima (i.e. directions of falling temperatures) on the monovariant lines. The diagrams were taken from ref. [144], where a detailed discussion is given.

### Basic thermodynamics and assessments of intermetallic systems

The intense work of the group on phase diagrams of intermetallic systems is also reflected in the publication of a number of assessments dealing with the ternary transition-metal-based systems Mo-Ni-V [138], Nb-Ni-V [139] Al-Ta-Ti [140], Fe-Mo-Ti [141], and Al-Co-Nb [142]. Moreover, based on the longstanding experience with Fe-Albased systems, the group got a chance to publish a book about "Selected Al-Fe-X Ternary Systems for Industrial Applications" [143].

One of the oldest thermodynamic rules is the so-called "Alkemade theorem". It allows to find the directions of falling temperatures along monovariant lines. This information is essential for the development of new alloys as it determines the course of the solidification path, which in turn gives information about the co-existing phases and the microstructure of the alloy. However, the original theorem is only defined for point phases, while most phases occur within extended composition ranges. Whether and how it can be applied in the latter case, e.g. by replacing the Alkemade lines by 'Alkemade regions' (Fig. 14), is discussed in a recent publication [144].

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