

Materials Research Department

No. 11 | 2019 **New Second Lange**

Research Insights and Information

Welcome to the 11th MRD Newsletter!

DEAR READERS,

we are delighted to welcome you to the 11th issue of the Materials Research Department's newsletter and to announce that from now on, the MRD newsletter will reappear regularly, with two issues each year. In the present issue, RUB's and MRD's new members will introduce themselves and their current research activities in the field of materials science and engineering.

Like all other previous newsletters, this 11th issue is accessible through the MRD website (http://mrd.rub.de/ reports/). We are always looking forward to receiving feedback and we welcome all of your suggestions for the next newsletter.

Enjoy reading,

P. Aleithe, R. Drautz, G. Eggeler, A. Marquardt

MRD today

The Materials Research Department (MRD) at Ruhr University Bochum (RUB) represents the interdisciplinary research field of Materials Science and Engineering (MSE), which focuses on the invention of new materials and on the development of new technologies in materials science with the objective, to help mastering the grand challenges of the future in the areas of energy supply, environment and climate protection, health, transport and mobility. In an interdisciplinary approach to materials science and engineering, more than 70 scientists from the faculties of chemistry and biochemistry, civil and environmental engineering, electrical engineering and information sciences, geosciences, history, mathematics, medicine, mechanical engineering and physics at RUB and from all leading research centers in NRW (e. g., German Aerospace Center (DLR), Forschungszentrum Jülich, Max-Plank-Institut für Eisenforschung and Max-Plank-Institut für Kohlenforschung) join forces within the MRD.

For this close collaboration MRD provides a platform for the scientists to exchange ideas, to develop new materials research strategies and to share advanced research infrastructure. The central research facility for materials science at RUB, the Center for Interface-Dominated High Performance Materials (ZGH, founded in 2012), provides access to advanced research equipment including analytical transmission electron microscopy (analytical TEM) and 3D atom probe tomography (3D APT) to all MRD members and associated scientists. RUB's Interdisciplinary Centre for Advanced Materials Simulation (ICAMS, founded in 2008) covers the principal theoretical and modelling aspects of advanced scale-bridging materials research.

RUB

Materials scientists at RUB are active in several research fields; strongholds presently include shape memory materials, high-temperature materials, plasma treatments of surfaces and catalysts for energy conversion.

MRD Board and Central Activities

The Materials Research Department is led by a board which was elected for two years (2018-2019) by all MRD members. The present board members are: Peter Awakowicz (Electrical Engineering), Anjana Devi (Chemistry), Ralf Drautz (ICAMS), Gunther Eggeler (Mechanical Engineering), Rebecca Janisch (ICAMS), Alfred Ludwig (Mechanical Engineering), Lukas Mai (Chemistry), Axel Marquardt (Mechanical Engineering), Jürgen Schreuer (Geosciences), Wolfgang Schuhmann (Chemistry) and Andreas Wieck (Physics). Lukas Mai and Axel Marquardt represent Ruhr University Bochum's young materials scientists in the MRD board and as one of their first important activities, they have organized the first Young Materials Researchers Day (YMR Day), which took place on December 3, 2018.

70 young materials scientists from MRD gathered to present and discuss their current research in talks and posters and exchanged ideas for upcoming MRD activities for young scientists in a workshop.



Participants of the first Young Materials Researchers Day on December 3, 2018

MRD's target agreement

In 2018, the MRD signed a target agreement with the RUB rector's office which highlights a number of objectives for the time period up to 2020. In 2020, there will be an intermediate assessment and in case this is successful, the agreement automatically extends for another three years until 2023. The rector's office supports the MRD by providing financial support for two 30-hours science management positions. Since summer 2018, the two MRD science managers, Pia Aleithe and Axel Marquardt, take care of all administrative and planning tasks which enables the day-to-day business of the MRD.

In 2018, all objectives highlighted in the target agreement between the MRD and the rector's office for the first three-year period

of the contract have been reached as planned. These include MRD's mission to foster internationalization activities by sending out young materials researchers to partner universities abroad. In 2018, more than 30 young materials researchers had the opportunity to spend time in research environments abroad to expand their horizon and perspective.

Two Alexander von Humboldt (AvH) Postdocs and one prestigious AvH Research Award Winner were successfully supported/ proposed by MRD members. Prof. Michael Mills from Ohio State University, the AvH Research Award Winner, will visit the Institute for Materials and ICAMS for six months in 2019/20. The MRD also makes



The two MRD science managers, Pia Aleithe and Axel Marquardt

an effort to renew existing and initiate new Memoranda of Understanding with partner universities, these activities are presently still ongoing.

Materials Chain International Conference

In close cooperation with the University Alliance Ruhr's flagship program Materials Chain, the MRD organized the second "Materials Chain International Conferece" (MCIC 2018). The conference took place from November 12 to 14, 2018 and was held at Ruhr University Bochum's Convention Center. More than 190 national and international participants, including eleven international invited speakers, presented their current research in 41 talks and 84 posters, exchanged ideas on future research projects, and used the conference to expand and maintain their research network. The international, professional exchange between the scientists of the MRD and scientists from other countries was much enjoyed by all participants. Among the participants were Professor Evelyn Hu (Harvard, Cambridge, USA), Professor Michael Moody (University of Oxford, Oxford, UK), Professor Aaron Stebner (Colorado School of Mines, Golden, USA), Professor Stefano Curtarolo (Duke University, Durham, USA), Professor Ichiro Takeuchi (University of Maryland, College Park, USA) and Dr. Robert Kostecki, (Lawrence Berkeley National Laboratory, Berkeley, USA).



Participants of the 2nd Materials Chain International Conference (MCIC 2018), November 3, 2018.

Research Center ZGH

Former MRD speaker Alfred Ludwig and ZGH's managing director Janine Pfetzing-Micklich will soon be able to inaugurate the new research building "Center for Interface-Dominated High Performance Materials" (ZGH) after several years of planning the building, surveying the construction work and coordinating all activities associated with identifying, requesting and setting up the new ZGH research equipment. To materials researchers at Ruhr University Bochum, who contribute to ZGH's research objectives, the ZGH will provide access to advanced characterization equipment including a high resolution cs-corrected TEM and a 3D atom probe. The ZGH will also host the MRD Science Management Office.

Higher Efficiency in Additive Manufacturing

Prof. Dr.-Ing. J. T. Sehrt

Nowadays, laser powder bed fusion of metals (PBF-LB/M) is one of the most requested additive manufacturing processes for the direct manufacturing of metal parts in the industry. During the PBF-LB/M process, thermal energy of one or multiple lasers selectively fuses regions of a metal powder bed.

One of the major disadvantages of PBF-LB/M is the low productivity on whose increase the chair for Hybrid Additive Manufacturing (Ruhr University Bochum) is working in cooperation with the Institute for Particle Technology (TU Braunschweig) within the DFG SPP 2122 "Materials for Additive Manufacturing". Recently, more and more PBF-LB/M machines are equipped with bigger build envelopes, multiple lasers and/or high power laser systems in order to increase process speed. Therefore, the approach here is not to focus on the machine itself but on the material. The main aim is to develop powders for PBF-LB/M, which have an increased absorptivity of the laser light and improved heat transfer capabilities during the process.

In this context, there is little preparatory work that starts directly at this point. Tolochko a) et al. [1] investigated the absorptance of singlecomponent powders and two-component powder mixtures suitable for PBF-LB/M of metals and polymers in a static experimental setup and environment. They c) figured out that the greater the absorptance of a powder material is, melt the powder.



Figure 1: SEM images and EDX analyses of a) 1.4404 raw material b) 1.4404 and CB c) 1.4404 and SiC

After coating the surface coated powders and the base feedstocks, were processed on the additive manufacturing system EOS M 100. The hatch distance was kept constant at 0.07 mm and the layer thickness was kept constant at 0.02 mm. The scan speed varied in five steps between 661.6-992.4 mm/s and the laser power varied in five steps between 61.7-92.5 W.

When looking at the weld beads on the top surfaces for same energy densities, a difference in the melting and consolidation behavior can be observed. This can also be seen in selected micrographs of the three different ans that faster process parameters (higher scanning speeds, bigger hatching distances and/or increased layer thicknesses) can be used for at least SiC-modified I.4404 stainless steel in order to achieve dense parts at high process efficiency.

It can also be observed that not only the amount of the volume energy density is of importance but also the parameters themselves. At the same volume energy density values of 66.6 J/mm³, samples with increased scanning speed and laser power (cf. Figure 2b) achieve higher densities compared to those one with decreased

> scanning speed and laser power (cf. Figure 2c). However, details of a potential change in the microstructure of the material and other properties such as the mechanical behavior will be investigated shortly to substantiate the possibilities of higher process efficiency in additive manufacturing by improved materials.

The chair Hybrid Additive Manufacturing (HAM) was established at Ruhr University Bochum in 2018 and focuses on the further development and merging of the two areas "hybrid" and "additive manufacturing". This combination offers great potential for future hybrid material developments in the field of ad-

ditive manufacturing, both in the academic environment and in industrial applications. The main research areas are: 1.) Extension of material selection by hybrid materials, 2.) Strategies for reproducible and robust hybrid additive manufacturing and 3.) Widening the understanding of the processes. In addition to these selected research areas, the goal is to manufacture components with application-specific properties and high quality.



the less energy output of the laser is necessary in order to sinter or melt the powder. Figure 2: Micrographs of 1.4404 and its 1.4404 composite materials after PBF-LB/M with different process parameters (*highest density values at 1.4404+SiC material) a) micrographs at Ev = 99.9 J/mm³, v = 661.6 mm/s, P = 92.5 W b) micrographs at Ev = 66.6 J/mm³, v = 992.4 mm/s, P = 92.5 W c) micrographs at Ev = 66.6 J/mm³, v = 827.0 mm/s, P = 77.1 W

To enhance the light absorption stainless steel (I.4404) powder was coated with silicon carbide (SiC) on the one hand and carbon black (CB) on the other hand. The coating quality of the powder was determined by using an SEM with an attached energy-dispersive X-ray spectroscopy (EDX) for quantification of elements. Figure I shows the raw material and two manufactured composites. 1.4404 powders after PBF-LB/M with different process parameters (cf. Figure 2). It can be seen that SiC and CB have a significant influence on the material processing behavior and therefore on the processing parameters. The SiC-modified stainless steel 1.4404 always shows the highest achieved densities - even higher than those of the reference stainless steel 1.4404 which was made for the PBF-LB/M process. Conversely, this me-



Group of Prof. Dr.-Ing. Jan T. Sehrt

Reference

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Prof. Dr.-Ing. Jan T. Sehrt; © RUB, Marquard

Prof. Dr. D. Balzani

Multiscale simulation of micro-heterogeneous metallic materials

The design and optimization of new materials can be significantly accelerated by incorporating computational simulation. As a result, either a more detailed understanding of how materials function can be achieved, or a computational optimization of e.g. material components can be made accessible. Aside from reliable materials models describing the mechanical response of the material's components, an essential prerequisite is a robust and efficient numerical scheme for the calculation of the partial differential equations governing the mechanical equilibrium. Since many modern materials, such as multiphase steel or metal matrix composites, make use of complex microstructures, scale-coupled modeling becomes important.

A suitable approach is the FE² method, where both macroscopic and microscopic simulations are performed using the Finite Element method (FE) and coupled by scale-coupling conditions. The major steps of the method are as follows: At each integration point of a macroscopic FE calculation, where, e.g., a sheet metal forming process is simulated, an additional microscopic simulation is performed by defining a representative volume element (RVE) and applying boundary conditions in terms of the macroscopic deformation state. After solving the microscopic boundary value problem, the resulting microscopic distribution of stresses is homogenized and returned as macroscopic stress to complete the macroscopic simulation. A schematic illustration is provided in Figure I.

The main challenge of this method is to overcome the burden of its large computational effort and thus, more efficient numerical strategies become essential. Most promising is the elimination of an unnecessary complexity of the microscopic problem. A method



Figure I: Schematic illustration of FE² scheme.

Thanks to the special integration scheme a speedup factor of over 100, compared to a conforming FE dis-cretization, could be realized. has been developed to construct artificial but statistically similar RVEs (SSRVEs) based on minimizing the deviation in a statistical sense of the microstructure morphology of the SSRVE compared to real microstructure data, see [1, 2]. Thereby, a significant reduction in the computing time by a factor of over 10000 can be realized. A new approach to further reduce the computing time and memory requirements, even if real microstructures are considered as RVE, is currently developed at Ruhr University Bochum's chair for Continuum Mechanics. Based on an optimized scheme for the volumetric integration, which directly exploits the voxel-based input data, the number of unknowns can be significantly reduced while keeping the accuracy. As an example, see the enlarged detail of Figure 2 (left), where the integration domains of a hard metal microstructure are depicted. The input data in terms of micro-CT voxel data has been provided by Arne Röttger (Chair of Materials Engineering, Ruhr University Bochum).

The major advantage of the FE² method is its major challenge at the same time: while it is directly possible to include mechanical phenomena acting on the microscale, these phenomena must be modeled accurately to compute a reliable macroscopic behavior. In the case of hard metals, whose wear-resistance performance is mainly governed by surface spalling, microscopic fracture processes have to be accurately simulated. Current research in the Continuum Mechanics group addresses this issue. Based on an extension of the eigenerosion approach in [3] to finite



Figure 2: Left: Simulated cracks (in gold color) through a hard metal microstructure consisting of a ceramic phase (green) embedded in a metal matrix (grey), which result from cyclic loading; the zoomed region illustrates the special Finite-Cell-based integration domains. Right: Contour plot of von Mises stresses in the cracked microstructure.

strains and elasto-plastic materials, the crack propagation due to cyclic loading can be simulated, see Figure 2 (left), and the accompanied mechanical fields in the microstructure can be studied, see Figure 2 (right). In the case of Dual-Phase (DP) steel, which consists of a martensitic phase embedded in a ferritic matrix phase, graded properties have already been observed within the ferrite, see [4]. These distributed properties mainly result from diffusion processes taking place during the production when the originally austenitic phase transforms to martensite. Following the approach in [4], a distributed modification factor is initially computed based on the plastic strains resulting from an initial volume jump of the martensite which is associated to the phase transformation. Figure 3 shows the associated RVE and the distribution of the amplification factor which is used to modify the associated yield response in the ferrite. Only by including these distributed properties it is possible to obtain a macroscopic response which is in line with experiments.



Figure 3: Left: Discretization of real microstructure of a Dual-Phase steel. Right: Simulated modification factor used for the distributed yield properties in the ferritic matrix.



Group of Prof. Dr. D. Balzani

A few lines on who the author is and what the group does

I am Full-Professor for Continuum Mechanics in the Department of Civil- and Environmental Engineering and the Department of Mechanical Engineering at Ruhr University Bochum since 2017. Before, I was an Open-Topic Full-Professor for Mechanics at Technische Universität Dresden since 2014. I received my doctoral degree at TU Darmstadt in 2006 and my habilitation from the University of Duisburg-Essen in 2012.

In between I served as substitute professor at Leibniz University Hannover from 2009 to 2010 and visited the California Institute of Technology as visiting associate from 2010 to 2011.

In my group, we develop new numerical methods and models to reliably simulate micro-heterogeneous materials at different scales to enable an accelerated and optimized design of new materials. Our focus is on the incorporation of graded properties in single microscopic phases, fracture at the microscale, as well as uncertainties resulting from e.g., microstructure variation. Especially the effect of static and dynamic macroscopic loading on the microscopic mechanical fields and vice versa are of central interest.

Aside from metallic materials, we develop computational models for other materials such as soft biological tissues, textile membranes, or reinforced concrete.

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Prof. Dr. Daniel Balzani ©Katja Marquard

Atomic-scale characterisation of electrocatalysts for sustainable energy conversion applications



Figure 1: a) Working principle of atom probe tomography, and b) atom probe located in ZGH.

With the global population predicted to double by 2070, and with the energy requirements of developing nations increasing significantly, access to affordable and renewable energy is one of the cornerstones of continuing global prosperity and economic growth. Most renewable energy devices and systems use catalyst materials to increase energy conversion rates. The morphology, composition and electronic structure of active sites and chemical species within the topmost atomic layers of electrocatalysts are crucial in the activity and selectivity of electrochemical reactions. In order to make technological promises reality and to achieve meaningful environmental impact, we must fully understand the state of individual atoms within the surface layers of the electrocatalysts in order to link fabrication, structure and properties. To date, it has not been possible to undertake a full three-dimensional (3D) structural and chemical characterisation of the topmost atomic layers of the electrocatalysts. This has hindered a complete evaluation of the contribution made by individual atoms in this extended zone to the interplay of catalytic activity, selectivity and stability in several important chemical reactions such as the oxygen reduction/evolution reaction (OER) for water electrolysis.

Thus, there is an urgent need for a new approach to the characterisation of catalyst materials to resolve individual atoms in 3D. Recently we started observing the structures of catalysts by atom probe tomography (APT), a non-routine characterisation technique for catalyst materials. APT, which combines field ion microscopy with mass spectrometry, provides a uniquely powerful insight into the 3D atomic-scale chemistry and structure of materials. APT analysis requires needle-shaped samples with a tip diameter of 30-100 nm. Surface atoms are field-evaporated by a combination of constant voltage and either a high voltage pulse or a laser pulse, as illustrated in Figure 1. Then the field-evaporated ion is projected on a single-ion-sensitive detector which records its x-y-z coordinates, and the time between the applied pulse and arrival of the ion, allowing a built-in mass-to-charge spectrometer to measure the mass-to-charge ratio. A 3D APT reconstruction can be achieved with individual atoms spatially and chemically resolved.

In recent work of the group "Characterisation of High-Performance Materials at Atomic Scale", an approach that combines APT with X-ray photoelectron spectroscopy (XPS) was deployed to measure the electronic state and atomic-scale surface structure and chemistry of iridium anodes for water electrolysis [1]. Metallic iridium and its oxides exhibit the best combination of activity and stability towards a sluggish oxygen evolution reaction (OER) at the anode for water electrolysis (under acidic conditions). A range of powerful in-situ chemical spectroscopy and surface techniques have provided valuable information on the surface species that are present during the OER. However,

simultaneously performing direct and surface-sensitive measurements during electrochemical reactions remains a challenge, such that there is a lack of current consensus on the nature of the surface state of IrO_x and surface species.

By using the new combined approach, we revealed that both activity and stability are improved at the beginning of reactions. As the anodic oxidation proceeds, the activity decreases and the stability increases. Interestingly, we observed small oxide particles with an O to Ir ratio of I:I along with loosely bound hydroxy-groups and water molecu-

Water electrolysis



Figure 2: Sketch of a water electrolyzer

les forming at the triple junctions of grain boundaries after a short time of anodic oxidation. The non-stoichiometric Ir-O species with hydroxy-groups and water molecules explain the high electrocatalytic activity. These metastable Ir-O species gradually transform into IrO₂, giving rise to the decrease in activity and the increase in stability. Gaining such important insights will enable us to overcome the current obstacles to knowledge-based





Figure 3: a) Schematic of the iridium sample, and b) APT data of iridium oxides formed by anodic oxidation for 4 h, 69 h and 120 h

catalyst design and provide a much-needed rational guide for OER catalyst optimisation. We believe that the combined approach will stimulate an entirely new field of atomic-scale surface species analysis.

A few lines on who the author is and what the group does

Jun.-Prof. Dr. Tong Li is leading a research group of characterisation of high-performance materials at atomic scale in the center for interface-dominated high-performance materials (ZGH) at Ruhr University Bochum.

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Jun.-Prof. Dr. Tong Li

Investigating fundamental aspects of high entropy alloys

Traditional engineering alloys commonly consist of a base element whose properties are altered by small additions of other elements, e.g., a small quantity of C is alloyed to the base element Fe in steels to improve its strength, and this alloy can be further made corrosion resistant with small additions of Cr and Ni. Recently, a novel class of metallic alloys consisting of many elements (\geq 5) without any principal element and referred to as "high-entropy alloys" (HEAs) has been introduced. The term "high-entropy" is based on the hypothesis that the high configurational entropy of these alloys may stabilize simple solid solutions against the formation of intermetallic phases. Therefore, one definition of HEAs is that these alloys are single-phase and compositionally complex solid solutions containing five or more elements in near-equiatomic proportions.

This new design of alloys with no principal element opens up a huge multi-component space to discover new alloys with interesting properties and a significant technological potential. Moreover these compositionally complex solid solutions are raising challenging scientific questions: How to describe solid solution strengthening in these complex alloys? Is there anything peculiar about the way that dislocations move in single-phase HEAs where the chemical environment around a dislocation changes over the length scale of the Burgers vector? Are there unusual deformation mechanisms taking place in HEAs? Do they exhibit superior properties compared to conventional alloys?

The current focus of the research group "Microstructure of Materials" at Ruhr University Bochum is to investigate these fundamental aspects in single-phase HEAs such as the face centered cubic (FCC) CrMnFeCoNi alloy, see [1, 2]. This HEA has been reported to exhibit fascinating mechanical properties. For example, two tensile stress-strain curves obtained at 20 °C (red) and -196 °C (blue) for the CrMnFeCoNi HEA are shown in Figure I (left). A comparison of these two curves allows to conclude that not only CrMnFeCo-Ni does show an excellent strength/ductility combination, but these properties improve at cryogenic temperatures where most conventional alloys change from ductile to brittle. On the one hand, the increase of strength with decreasing temperature could recently be rationalized in the light of a solid solution strengthening model developed for FCC



Figure 1: Microstructural evolution and critical stress for deformation twinning in the CrMnFeCoNi HEA. (Left) Representative stress strain curves obtained at 20 °C and at -196 °C. The letters a to b highlight the strain levels at which additional tensile tests were interrupted. (Right) Corresponding TEM micrographs (bright and dark field images) show the evolution of microstructure at -196 °C (blue frame) and 20 °C (red frame).

HEAs [3]. On the other hand, it remained to clarify why the ductility of this alloy improves at cryogenic temperatures.

To identify the key microstructural aspects responsible for this effect, the microstructural evolution during tensile deformation was investigated by transmission electron microscopy (TEM). At -196 °C, the TEM micrographs (framed in blue) reveal that the plastic deformation is initially accommodated by planar glide of dislocations at low applied strains (~ 2 %, see Figure 1a). However, after 7 % strain, an additional deformation mechanism occurs, namely, deformation twinning, whose onset is shown in Figure 1b. Here, the twins are very thin and can be recognized with their bright contrast. At 20 °C, similar microstructures were observed but deformation twinning was found to be triggered close to fracture, see Figure 1d. Based on these results, the onset of deformation twinning is highlighted with a black dashed line in Figure 1. Here, it can be clearly seen that a critical stress of 720 MPa must be reached before deformation twinning occurs. When it does, new twin interfaces are introduced during deformation and they constitute barriers to the motion of dislocations like grain boundaries.

In other words, the mean grain size of the alloy is dynamically reduced with increasing plastic strain which is why this phenomenon is also referred to as "dynamic Hall-Petch effect" in the literature. This effect promotes a large work hardening rate (slope of the stress-strain curve) which allows to delay necking and to enhance the uniform elongation before fracture. As this critical twinning stress at 20 °C is only reached close to fracture, this mechanism does not contribute to the work hardening rate which implies a low ductility. However, at -196 °C, as the yield stress is much higher than that at 20 °C, the critical twinning stress is reached

a much lower strain, promotes a large work hardening rate which in turn enhances the ductility. Thus, it can be seen that by using transmission electron microscopy (TEM) to investigate the microstructural evolution during tensile deformation, it was possible to shed light on key elementary deformation mechanisms responsible for the outstanding mechanical properties of the CrMnFeCoNi HEA at cryogenic temperatures.

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Jun.-Prof. Dr. Guillaume Laplanche

Design of high-temperature shape memory alloys

Prof. Dr. R. Drautz, PD Dr.-Ing. J. Frenzel

Shape memory alloys are fascinating materials. They are able to recover their original shape after a strong deformation. Shape memory alloys are smart materials. They can be used as actuators, which can displace structures or masses, and control systems. They have applications in medical, aerospace, automotive, construction and environmental sectors. The Materials Research Department has a long-standing expertise in shape memory alloy research and is among the world leaders in this field today.

The shape memory effect derives from a martensitic transformation, where a high-temperature austenite phase transforms into a low temperature martensite on cooling. The reverse transformation occurs upon heating. Most shape memory materials are based on Ni-Ti-alloys. Ni-Ti is an atomically ordered material and its shape memory effect has a great sensitivity to alloying additions. The development of Ni-Ti-based alloys for applications at high temperature above 100 °C is difficult and possible alloying elements are rare and expensive.

Several groups are currently competing in their search for novel shape memory alloys for high-temperature applications. Recently, we have studied new Ti-Ta-based materials which provide a significantly improved functional performance. In contrast to other materials, such as Ni-Ti-based alloys, our Ti-Ta-based alloys are sufficiently ductile such that semi-parts like bars, rods, sheets and wires can be easily prepared by conventional processing techniques. Figure 1 exemplarily documents the functional behavior of a Ti-Ta-based spring actuator which was prepared at Ruhr University Bochum. The spring is mounted in a test rig where it is loaded with a weight. During direct current heating, the actuator transforms back

into the high-temperature phase. In parallel, the spring contracts, trying to re-establish its prior geometry.

The atomically disordered Ti-Ta system forms a good basis for the design of a novel shape memory alloy. The transformation temperature in Ti-Ta decreases with Ta content and for a high-temperature shape memory alloy, moderate Ta contents of about 25 at% are desirable. At these compositions the ω -phase competes with the martensite and austenite phases. During transformation between the austenite and martensite phases, the ω -phase precipitates with catastrophic consequences for the shape memory effect. After only a few cycles the shape memory effect is lost. This poses the design challenge for a new high-temperature shape memory alloy: suppress the formation of the ω -phase while maintaining the beneficial properties of the Ti-Ta-base material.

Employing high-throughput density functional theory calculations together with physically and chemically transparent descriptors, Alberto Ferrari, Jutta Rogal and Ralf Drautz (ICAMS) screened the periodic ta-



igure 1: Thermally induced shape memory effect in a Ti-Ta-based high-temperature shape memory spring actuator during direct current heating. Temperature distributions in the spring are monitored by infrared thermography (see insets).



Figure 2: No degradation of the shape memory effect is observed when cycling the austenite-martensite transition with a novel high-temperature shape memory alloy. The composition of the alloy was designed on the basis of parameter-free ab initio calculations. a) Cyclic DSC analysis of a conventional, unstable, Ti-Ta-base alloy.

b) Cyclic DSC-data of the new Ti-Ta-based high-temperature shape memory alloy.

ble for possible alloying additions to the Ti-Ta-base alloy that would suppress the formation of the ω -phase. This search has resulted in several suggestions for new alloy compositions.

At the Institute for Materials (IfM), Alexander Paulsen, Jan Frenzel and Gunther Eggeler prepared the most promising alloy out of the theoretically suggested compositions. As displayed in Figure 2, the new alloy maintains a stable shape memory effect for many cycles. Transmission electron microscopy analysis by Dennis Langenkämper and Christoph Somsen confirmed that the theoretically predicted alloying additions suppress the formation of the detrimental ω -phase. The novel, computationally designed material therefore appears to be an excellent material for high-temperature shape memory applications.



Towards unravelling nanoparticle reaction dynamics Prof. Dr. K. Tschulik, J. Linnemann, K. Wonner

Commercial applications of nanoparticles (NPs) have already captured the market in many product areas such as medicine, food and cosmetics as well as in further sectors. e.g. industrial chemistry. Nanomaterials exhibit, compared to the respective bulk materials, distinctive properties such as enhanced catalytic activity and antibacterial effects due to the high surface-area-to-volume ratio and the altered electronic structure. The new 'playground' of possibilities to develop and improve functional materials also comprises challenges. The current lack of a profound understanding of function-property relations does not only hinder a rational materials design, it also results in unknown environmental and biological interactions of the material's components after the product life cycle. Hence, gaining an improved understanding of the induced changes of nanoparticles during their application and after their disposal is essential to optimize their utilization and minimize undesired environmental aftermaths.

The latter issue can be addressed by means of characterizing the persistence behavior and possible reprocessing treatments of nanomaterials. To this end, one needs to identify which kinetics, reactions and final appearances are expected for nanoparticles in a specific surrounding medium, such as biological liquids or surface. Electrochemical measurement techniques generally provide the ability of triggering reactions on solid/ solution interfaces (electrode/electrolyte) by the controlled alteration of the electrode potential. Furthermore, the resulting current is a direct measure of the reaction rates of the triggered electrochemical processes.

However, there are still two major difficulties in researching reactivity-related processes at the nanoscale. Firstly, only ensemble properties of a whole electrode are characterized. Hence, only integral information of nanoparticles (e.g., size-distribution) is acquired, which is further influenced – to a typically unknown extent by substrate materials and additives used for electrode preparation. Accordingly, it is problematic to extract valid structure-property relations. Secondly, many elaborate ex-situ and in-situ



Figure 1: Dark-field microscopy images of silver and resulting silver chloride nanoparticles attached to an electrode in potassium chloride solution at different potentials recorded during a CV scan. The potential is increased to a specified value capable of oxidizing silver and subsequently decreased to a more reductive potential where elemental silver is formed. The nanoparticles are visible due to LSPR. techniques only provide information on the state before and after the process in question, but not on the reaction dynamics. In sum, new analytical approaches are urgently needed to investigate the reaction dynamics of individual nanoparticles.

Recently, the simultaneous combination of hyperspectral dark-field microscopy and cyclic voltammetry (CV) have allowed for the operando investigation of individual reacting nanoparticles as part of a particle ensemble attached to an electrode [1-3]. Many metallic nanoparticles interact with light due to localized surface plasmon resonance (LSPR), an effect describing the coherent oscillation of free valence electrons of the particles' conduction bands excited by electromagnetic radiation of a suitable wavelength. Therefore, information about shape, surface conditions and size of nanoparticles can be extracted from scattering spectra of the particles. Dark-field microscopy, in which scattered light instead of transmitted light is used for imaging, is applied for spatially-resolved characterization of the LSPR of nanoparticle-coated electrodes (Figure 1) circumventing Abbe's diffraction limit. As shown in Figure 2b, hyperspectral measurement equipment additionally allows us to detect scattering intensity as a function of the wavelength in the UV/IR range with high temporal resolution. Comparing the current response with the observed change in the relative intensity of an individual nanoparticle's scattering spectrum (Figure 2a), rigorous chemical changes become obvious, which cannot be identified solely from the

current signals. For the case of silver nanoparticles, which are, e.g., applied in functional clothing due to their antibacterial properties, we found that they reversibly react to silver chloride and possibly form silver-oxo-species at even more positive potentials (> 1.15 V) in chloride solutions. In the presence of chloride, a comparatively small release of silver ions is therefore expected, in contrast to the large local silver ion concentrations one would obtain without chloride in the nanoparticle surrounding. This likely reduces toxic effects of silver nanoparticles on cells, but may in turn result in very long particle lifetimes in biological and environmental fluids.

Correlated characterization techniques to study reaction dynamics of individual nanoparticles during proceeding reactions offers the possibility to pave the way for the knowledge- and insight-driven development of nanomaterials in several areas, such as electrocatalysis. The possibility to assess the material's intrinsic reaction behavior, allows to establish actual structure-property relations in contrast to the conventional characterization of ensemble properties of many particles together with additives. Unravelling this potential by pushing the limits of electrochemical and spectro-electrochemical characterization to the single nanoparticle level is the essential research interest of the Chair Analytical Chemistry II at Ruhr University Bochum so as to eventually help resolve the unexplored secrets associated with nanoparticle design, synthesis, degradation, and uses in electrocatalysis, biomedical, and energy storage applications.

A few lines on who the author is and what the group does

The Chair of Analytical Chemistry II develops advanced electroanalytical approaches to study reactions of and at functional materials, particularly at the nanoscale. Our aim is to link intrinsic material properties to reaction kinetics and thus gain in-depth physico-chemical insights into structure-activity relations, for instance in electrocatalysis and corrosion. We further develop new routes to control local mass transport by application of magnetic fields, for instance to produce patterned electrodeposits.



Figure 2: CV of a silver nanparticle-coated platinum wire electrode in aqueous 50 mM potassium chloride solution: a) correlated plot of the applied potential (red), the relative intensity of the scattered light (blue) and the current (black) depending on the time and b) 3D plot of the corrected and normalized extinction spectra of a single nanoparticle.

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Shape memory polymers: How dwarfs set giants in motion

Functional materials play an increasingly important role in our everyday life. They appear, for example, as "intelligent" actuators and switches, which respond to an external stimulus such as light, temperature or mechanical stress/load. Among many materials used, polymers play a key role here. Photo responsive polymers, for example, can activate or tune specific functionalities upon receiving light with different intensities. Shape memory polymers, on the other hand, can recover an initial programmed shape upon changing the ambient temperature. zingly simple and effective at the same time: One inserts the sample into a solvent made of the small molecules of interest and waits.

The time necessary to reach a certain effect is tabulated via straightforward but carefully performed weight take-up measurements. The solvents required in this process are not fancy exotic molecules but easily available in the market. Examples are water, ethanol, or acetone. The researchers at RUB have shown that tiny amounts of these simple solvents, once penetrated into a shape memory material, can drastically influence the via molecular dynamics studies the mechanism behind this interesting effect: Small molecules are fast and jiggle around all the time, whereas polymeric molecules are large and "lazy". The small dwarfs, however, do not let the giants in peace but kick them incessantly. The giants wake up and become mobile. This is the beginning of the recovery process. Thank god, they are not hungry!

Prof. Dr. Fathollah Varnik







Figure 1: Left: A programmed shape memory sample is exposed to ethanol and recovers its original (shorter) length after 92 hours. Right: Molecular dynamics model of the material showing small molecules as gold spherical particles. The polymer character is made visible in the right by showing one of the large molecules. The fast moving small particles enhance the dynamics of polymeric molecules, thereby triggering shape recovery.

The researchers at the Ruhr University Bochum (Institute for Materials, Prof. Gunther Eggeler) have recently discovered that the recovery process of polymeric shape memory materials, which are made of rather large molecules, can be triggered by adding small molecules. The way this is achieved is amaglass transition temperature of the sample and thereby reduce the recovery temperature. As soon as this reaches the room temperature, the sample starts to regain its initial shape (Figure I). Colleagues from ICAMS (Theory and Simulation of Complex Fluids, ICAMS, Prof. Fathollah Varnik) have shown





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