RUHR-UNIVERSITÄT BOCHUM

RUB

MATERIALS RESEARCH DEPARTMENT



NO. 16

Materials Research Department



FOCUS ON: ADVANCED MATERIALS CHARACTERIZATION

Materials characterization is fundamental for materials science. It is the basis for insight and understanding and indispensable for the development of novel materials.

The 16th MRD newsletter showcases cutting-edge advanced materials characterization facilities and expertise in the MRD. Like all previous newsletters, this 16th issue is also accessible through the MRD website.

Enjoy reading,

R. Drautz and A. Devi MRD Speakers P. Aleithe and P. Maaß MRD Science Managers

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On the Cover: SEM Micrograph of a Deformed Gold Flake



TRANSMISSION ELECTRON MICROSCOPY

Understanding materials through their microstructure

My adventure with microstructural characterization started during my PhD studies in Poland. At that time, I was simply fascinated by the electron microscope itself: its complexity, performance, and possibility to "see atoms". During one of the discussions with my supervisor - Prof. Henryk Morawiec, we read the text of Mr Robert W. Cahn: "Studies of the interface structure and properties are the most striking of all changes in the practice of materials science and engineering, which will certainly have a major impact on the future of our science..." [Materials Today, Vol 2, Elsevier 1999]. That citation becomes my scientific guidance and a gate into the wonders of materials science where the microscope is just a tool to understand the materials through the study of their microstructure and its correlation with properties.

Microstructure refers to the microscopic description of the individual constituents of a material like the crystal structure (type and arrangements of atoms in a unit cell), chemical composition, size and morphology of grains, their crystallographic orientation (texture), presence of defects, their types, densities, and interactions. During fabrication and processing - the microstructure evolves,



and its components interact affecting the macroscopic behavior and physical properties. Knowing the microstructure is essential for the development, optimization, and safe use of advanced materials. One of the ultimate tools for microstructural characterization is a transmission electron microscope (TEM).

TEM is a research device which use an electron beam (which is transmitted through a specimen) to form an image. However, here is the most unique feature of the TEM: interacting with the ultrathin specimen electron beam cause simultaneous formation of two distinctive images: (i) a conventional image - forming in the image plane of the objective lens and (ii) an electron diffraction pattern forming in the back focal plane of the objective lens. That is up to the microscope operator to select which of the images are to be displayed and recorded for further analysis. It means that we can record an image showing us a grain, crystal or defect and a corresponding electron diffraction pattern which is essential for a detailed description of the analyzed feature. Modern instruments offer large variety of imaging modes: BF, DF, TEM, HR-TEM, BF-STEM, DF-STEM, NBD, CBED, spectroscopy modes: EDS, EELS, and 3D tomography, providing information about the structure and chemistry of the analyzed material. Often, many of these signals can be recorded simultaneously.

First electron microscope (build in 1936) offered resolution lower than that of light microscopes (light microscope resolution is typically about 200nm). Within next decades electron microscopes developed to the sub-angstrom resolution (below 70pm). That supreme resolution together with the wide range of structural information availability makes modern TEM's a high-end tool for the advanced characterization.



Figure 1: Ni-base superalloy

Advanced characterization of material is fast (to minimize the beam damage and specimen drift), precise (often the focused ion mill (FIB) prepared samples contain carefully selected microstructural features to be analyzed), and detailed (the instrument can simultaneously record signals from many detectors, or many complementary techniques is used to deliver best possible structural information).

Advanced microstructural characterization supported by scale bridging modelling is implemented to manufacturing, processing, and testing leading to better understanding of fundamental processes govern the service of advanced interface-controlled materials. Many excellent examples of advanced material characterization are published through the Collaborative Research Centre (CRC) Transregio 103 "From atoms to turbine blades – a scientific basis for a new generation of single crystal superalloys" [https://www. sfb-transregio103.de].



Figure 2: M23C6 carbide in Nicrofer alloy



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IN-SITU ALLOYING IN ADDITIVE MANUFACTURING

Assessing chemical and phase stability inhomogeneities by combining composition and phase maps

Additive manufacturing, in which a component is built layer by layer directly from a 3D CAD model, enables the rapid and resource-efficient production of highly customized and complex components. One manufacturing route used in particular for the processing of metals is the Laser Powder Bed Fusion (PBF-LB/M) process, in which metallic powders are locally melted by a focused high-energy laser beam, causing metallurgical fusion between the multiple layers of molten powder. The focused laser energy input leads to high temperature gradients and results in high solidification and cooling rates of the melt. These thermal conditions currently limit the materials that can be processed using PBF-LB/M, slowing the progress of additive manufacturing towards large industrial applications.

Because of this limitation, we are working on new materials that are PBF-LB/M-processable and also have improved properties, such as higher strength or corrosion resistance, compared to currently-available materials. However, alloy development is generally expensive due to the starting powdered material, which is produced using cost-intensive and time-consuming gas atomization. As a result, in-situ alloying (ISA) has recently gained popularity, where at least two starting powders (elemental or alloyed powders) are mixed prior to PBF-LB/M processing and then metallurgically fused during manufacturing. During PBF-LB/M, chemical inhomogeneities occur depending on the degree of difference in the chemical composition of the starting powders and the parameters used in the process. These inhomogeneities influence the local phase formation and thus the overall microstructure formation of the additively manufactured component, which, in turn, influences the emerging properties. The characterization of these inhomogeneous microstructures is essential for understanding the reigning process-structure-property correlations. To that end, we use a combination of different analytical techniques. Electron Backscatter Diffraction (EBSD) is used for local phase analysis and phase fraction quantification, and is accompanied by quantitative elemental mapping of the substituent elements using Energy dispersive X-ray spectrometry (EDS), allowing the phase information obtained from EBSD to be directly related to the local chemical composition. To quantify the phase-dependent chemical concentration of the interstitially dissolved elements such as C and N, Wavelength Dispersive X-Ray Spectrometry (WDS) measurements are additionally performed. We use the aggregated data from these investigations to quantify the degree of inhomogeneity, e.g. as a function of the alloy system or the energy introduced in the process, and also to establish a link between the phase formation and the local chemical composition. In this context, as indicated

in the flowchart below, we employ thermodynamic calculations to determine the local phase stability as a function of the local chemical composition, giving rise to the so-called stability maps. From this, transformation tendencies can be deduced, which is particularly important for mechanical behavior.

The analytical techniques employed provide a wealth of spatial information, certainly enough

to fully describe chemical and phase stability inhomogeneities. However, to go beyond their mere qualitative examination and comparison, we need description methods that condense the data into useful, physically meaningful descriptors. Drawing from spatial statistics, we employ statistical tools that can simultaneously characterize inhomogeneities thoroughly and provide deep insights into their physical context. These are variograms, covariograms and n-point probability functions, point-symmetric descriptors that present structural spatial variations with high information density. A good place to start explaining them is the variogram: it shows the difference in property values between all pairs of points separated by a given distance in a given direction. So, as shown in the flowchart, we use it to describe and understand the spatial variation of alloying element concentrations. Covariograms are similar, but display the covariance of the distribution of two variables. Fittingly, they can be deployed to characterize the segregation behavior of substitutional elements. Finally, n-point probability functions detail the extent and distribution of regions in a map. These regions are usually the phase domains. Further, the resulting stability maps can be subjected to the variogram analysis described above. The information collected and condensed by these descriptors casts light on the effect that the process variables exert on the microstructure, and, in turn, helps explain the emerging properties. Furthermore, the comprehensive statistical description makes these tools very attractive for the fields of Microstructural Reconstruction and Design.



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Figure 1: Combination of analytical techniques for the characterization of inhomogenous microsctructures

REFERENCES:

1 F. Großwendt, et al., Materials Science and Engineering: A (2021), 827, 142038 2 C. Cui, et al., Journal of Manufacturing and Materials Processing (2022), 6(4), 72 3 L. Becker, et al., Materialia, (2022), 22, 101393 4 L. Becker, et al., Materialia (2023), 28, 101720 5 S. Benito, et al., Materials Today Communications (2023), 34, 105016

ATOMIC-SCALE CHARACTERIZATION OF ELECTROCATALYSTS



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Using atomic probe tomography to get an insight into the 3D atomic-scale chemistry and structure of materials

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 the 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 (ORR/ OER) for water electrolysis.

Thus, there is an urgent need for a new approach to characterise catalyst materials. My group employs atom probe tomography (APT) to resolve individual atoms of electrocatalysts in 3D. APT is 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 Fig. 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 our recent work (DOI: 10.1021/ acscatal.2c03903), we developed a correlative approach with Professor Kristina Tschulik's group by combining APT with X-ray photoelectron spectroscopy (XPS) and electrochemical measurements to investigate the temporal evolution of oxidation state, thickness, morphology and elemental distribution of cobalt oxyhydroxides during OER. We reveal that the oxyhydroxide layer with the highest OER activity is 5-6 nm thick β -CoOOH(0001) film, consisting of stacks of nanocrystals; this explains the amorphous characteristic of active species formed on Co-based electrocatalysts observed by operando X-ray-based techniques. The interfaces between the $\beta\text{-CoOOH}(0001)$ nanocrystals accelerate the intercalation of water molecules and hydroxyl groups along β -CoOOH(0110) into slabs, enhancing the OER activity. As OER proceeds, the β -CoOOH(0001) nanocrystals grow into a monolithic β -CoOOH(0001) film along with the water deintercalation. The decreased number of interfaces serving as active regions most likely leads to a slight decrease in the OER activity, although the surface species are highly reversible. Overall, our study unprecedentedly unveils that in situ generated thin β-CoOOH(0001) layer undergoes dynamic morphological and elemental changes along with (de)intercalation of water molecules and hydroxyl groups during OER, which in turn alters OER activity. We demonstrate the strength of our multimodal characterization approach when seeking mechanistic insights into the role of structural and compositional evolution of hydrous oxides in activity during electrocatalytic reactions.



Fig. 1. a) working principle of atom probe tomography, and b) atom probe located in ZGH

 Figure 1: Look into the XPS-chamber



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X-RAY PHOTOELECTRON SPECTROSCOPY

Providing insights into bonding states and the growth behaviour of coatings

At the Research Department Plasmas with Complex Interactions an X-ray photoelectron spectroscopy (XPS) device is available for surface analysis. The instrument is located at the Chair for Experimental Physics II in the NB building on the RUB campus. Measurements in the context of research progress on campus are supported by the XPS instrument by providing insights into bonding states at the surface of coatings or materials. For example, this provides insight into the progression of growth behavior of coatings. In addition, depth profiling provides the opportunity to look deeper into the layer. Research on surface diagnostics is

currently being carried out in CRC 1316, which will provide information on the influence of atmospheric pressure plasmas on catalysts.

The operating principle of XPS is based on the extraction of electrons from a sample surface irradiated with X-ray photons. X-rays are generated when a beam of electrons with sufficient energy to promote transitions between atomic nuclear levels strikes an anode. The generated X-rays are directed to a monochromator where radiation with an energy of 1486.6 eV is selected. These X-ray photons are directed onto a sample. The interaction of the X-ray beam with the

> atoms of the sample leads to the excitation and extraction of electrons. The extracted electrons are collected in a detector where their kinetic energy is measured.

Each element is characterized by the binding energies of the electrons in the different atomic nuclei levels. The only elements that are not detectable in XPS are hydrogen and helium. Chemical bonding between atoms results in a shift in the binding energy position, allowing chemical analysis of the measured samples. This technique is referred to as ESCA (Electron Spectroscopy for Chemical Analysis).

X-ray photoelectron spectroscopy is performed using a Versaprobe spectrometer from Physical Electronics (PHI 5000 VersaProbe). Al Ka-radiation with an energy of hv = 1486.6 eV is produced at an aluminum anode. The measurement spot can be attached with diameters of 20 μ m, 100 μ m or 200 μ m. Standard measurements are performed with an inclination angle of 45° between the sample and the detector. Angles between 15° and 85° can be used for angle-resolved measurements. An ion gun with an argon source is adapted to allow sputtering of samples with energies between 20 V and 4 kV.

Three types of sample holders are available, the small one is a 1-inch circular holder, and the larger one is a 2-inch circular holder. Finally, there is an angle resolved specimen holder that can hold up to eight specimens. The circular specimen holders have masks that can be used to measure wafers or other solid specimens.



Figure 2: XPS-chamber located at the Chair for Experimental Physics II

MEASUREMENTS FOR PHYSICAL PHASE DIAGRAMS

Figure 1: Photograph of the

cryostat belonging to a Quan-

tum Design Physical Prop-

erty Measurement System, and the sample carrier of the

heat-capacity option.

Using a Physical Property Measurement System to control and modify a sample during a measurement

Many quantum materials exhibit intricate physical phase diagrams, where a slight change of an external parameter might make the difference between the material being a magnetic insulator or a high-temperature superconductor. This external parameter (so-called "tuning" parameter) can be the material composition, external pressure, or a magnetic field, to name the most common examples. We have investigated the intricate phase diagrams realized by tuning materials of the family of the iron-based superconductors using basic physical property measurements over the past years.

The electrical resistance is a basic property which, when measured at sufficiently high resolution, can signal almost any phase transition. In particular, its vanishing is a hallmark of superconductivity. In addition, magnetic susceptibility measurements serve to identify superconductivity, but also ferro- or antiferromagnetic phases. Measurements of the specific heat capacity are a prime method to assess a phase transition, since they help to quantify the entropy changes involved. The high-resolution measurement of the thermal expansion is also very useful to find and assess phase transitions. Overall, at least minor anomalies (such as peaks steps or kinks) will occur at a phase transition in all physical properties. When the phase lines have been found with the basic property measurements, more advanced techniques, such as diffraction or imaging, are used to identify the still unknown phases.

A widely-used, robust, reliable and high-precision machine for such measurements is a Physical Property Measurement System (aka "PPMS"), which has been pioneered by Quantum Design, Inc. It allows to control and rapidly modify the temperature and magnetic field environment of the



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Figure 3: Temperature-composition phase diagrams of various iron-based superconductors. All systems have a tetragonal and paramagnetic high-temperature phase. They exhibit an orthorhombic and antiferromagnetic, as well as a superconducting phase at lower temperatures. Ba(Fe,Co)₂As₂ shows an addtional nematic phase [1,2], (Ba,K)Fe₂As₂ features an extra "double-Q" magnetic phase [3] and strained Ca(Fe,Co), As, has a special mixed-phase region [4]. Phases were delineated and identified using a combination of basic property measurements, diffraction and microscopy.



sample, while different options enable the physical measurements, including electrical transport, magnetization, or heat capacity.

We have used physical property measurements to outline the composition-temperature phase diagrams of many iron-based superconductors [1]. In general, these phase diagrams look similar with superconductivity occurring in a dome-like area that peaks when an antiferromagnetic and orthorhombic phase is suppressed. However, variations of this theme hold clues for understanding of how these phases come to be. For example, whereas in some materials a tetragonal-to-orthorhombic structural transition coincides with an antiferromagnetic one, the two transitions split in others and the structural transition precedes the magnetic transition. This sparked the extremely active field of "nematicity" in these material systems, which we discussed [2]. Moreover, our investigations revealed a small pocket of a new exotic "double-Q" magnetic phase in one iron-based system and discovered superconductivity acts to suppress it again [3]. With up to four subtle phase transitions between 20 - 60 K, the combination of high-resolution thermal expansion, heat capacity and susceptibility measurement was indispensable for identifying the phase lines. Finally, we could identify a mixed-phase region in an extremely strained system [4].

All in all, basic physical properties allow to characterize in detail the average state of a material. Thus, they leverage their full power when highly homogeneous samples, most often single crystals, are under investigation. They are the basis, on which more advanced studies of electronic band dispersions, magnetic textures and propagation vectors, or quasiparticle excitation spectra-to name just a few - build.



Ba(Fe,Co)₂As₂

SC

8

strained

mixed

4

Ca(Fe,Co)₂As₂

12



REFERENCES:

1 Anna Böhmer und Andreas Kreyssig, Unkonventionelle Hochtemperatur-Supraleitung: Eisenbasierte Vielfalt, Physik in unserer Zeit 2/2017 (2017). DOI: 10.1002/ piuz.201701462 2 Anna E. Böhmer, Jiun-Haw Chu, Samuel Lederer and Ming Yi, Nematicity and nematic fluctuations in ironbased superconductors, Nature Physics 18, 1412 (2022) 3 A. E. Böhmer, F. Hardy, L. Wang, T. Wolf, P. Schweiss, C. Meingast, Superconductivity-induced reentrance of orthorhombic distortion in Ba,-,K,Fe,As,, Nature Communications 6, 7911 (2015) 4 A. E. Böhmer, A. Sapkota, A. Kreyssig, S. L. Bud'ko, G. Drachuck, S. M. Saunders, A. I. Goldman, and P. C. Canfield, Effect of biaxial strain on the phase transitions of Ca(Fe1, Co), As2, Phys. Rev. Lett. 118, 107002 (2017)

ION BEAM ANALYSIS IN RUBION

Quantitative characterization of materials with ion beams at the Central Unit for Ion Beams and Radionuclides (RUBION)



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Ion beam analysis (IBA) is a group of analytical techniques based on the detection of charged particles or photons emitted by the bombardment of a sample with high-energy ions. All IBA techniques are characterized by unique features, such as high accuracy and sensitivity, while simultaneously allowing the least-destructive and standard-less quantitative analysis in near-surface layers of samples of interest to many disciplines such as chemistry, biology, geology and archaeology. Hence, IBA is widely recognized as a strong, interdisciplinary field that utilizes Nuclear Physics knowledge and expertise in Materials Science.

The central unit of the Ruhr-University Bochum RUBION has an accelerator facility which is equipped for the application of almost all IBA techniques, namely RBS, NRA, NRRA (NRA in the presence of strong, narrow resonances in particular for hydrogen detection), PIXE (Particle-induced X-ray emission) and PIGE (Particle-induced γ -ray emission). In collaboration with various institutes of RUB and other universities in Germany and abroad, IBA and particularly RBS and NRA measurements are performed for the characterization of different kinds of samples – thin films of few nm or thick specimens of μ m, in-depth homogenous or layered ones.

Depending on the elements under investigation and the sample matrix, either RBS using 2 MeV alpha particles or NRA with 1 MeV deuterons is employed. These ion beams are provided by the 4 MV tandem accelerator (Fig. 1). In most cases, however, the application of both techniques is necessary for the analysis of a single sample, since these techniques are often complementary. As Figure 2 illustrates, RBS is ideal for probing of heavy elements in light or medium-Z matrices, while NRA is the most suitable one to detect the light elements, even if they occur in high- or medium-Z matrices.

Typical sample materials for which these techniques are particularly suited for the investigation of its stoichiometry are thin films deposited on substrates like Si wafers (Fig. 3). Layers of metal oxides, carbides, or nitrides as well sulfides are the most frequently measured materials. The following small selection of materials analysis demonstrates the possibilities of the techniques provided by RUBION. In a recent work on CVD Grown Tungsten Oxide for sensing applications RBS together with NRA was utilized to determine the thin film thickness and composition [1]. Another example is a study of cesium lead bromide perovskites as light emitting material. For the sample characterization RBS made the contribution of the molecular ratios of the thin films [2]. In the case of material libraries produced by a reactive magnetron codeposition process, the oxygen content of La-Co-O thin-film libraries were investigated using a 4He ion beam with an energy of 3 MeV [3].







Figure 2: RBS is ideal for probing heavy elements, while NRA is most suitable to detect light elements.



Figure 3: Thin films deposited on Si substrates can be investigated using RBS and NRA.

REFERENCES:

1 Wilken, M., et al., Small 2023, 19, 2204636 2 Pourdavoud, N., et al., Adv. Mater. 2019, 31, 1903717 3 Piotrowiak, T.H., et al., Adv. Eng. Mater., 25: 2201050.





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