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“Microscopy and Materials Characterization”

Abstract booklet

October, 12 - October 13, 2022

Dresden, Germany

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“Microscopy and Materials Characterization”

The European School will be dedicated to the exciting field of Microscopy and Materials Characterization. The goal of the European School is to bring together PhD students and young scientists from Physics, Chemistry, Materials Science and Computer Science, to present and to discuss their research topics. The European School will include two invited talks from experienced scientists, a round-table discussion with entrepreneurs and scientists working for a start-up, and oral presentations of each participant.

All PhD students and young scientists are invited to attend the Correlative Materials Characterization (CMC) workshop in Dresden on 13 – 14 October 2022 with opportunity to present their studies as a poster.

Venue of the European School and CMC workshop:

October 12-14, 2022, Dresden, Germany
Pfotenhauerstraße 108, 01307 Dresden, Germany
Max Planck Institute of Molecular Cell Biology and Genetics (MPI-CBG)

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Ehrenfried Zschech, deepXscan Dresden

Pawel Zieba, IMIM PAN Krakow

Olivier Thomas, Aix-Marseille University

Jan Neuman, NenoVision Brno

Highlights

- Invited introduction talk “Deep Learning – a birds eye view on what it is and why it is so successful”, Florian Jug, HT Milano, Italy.
- Introduction about Correlative Materials Characterization – Concepts and examples: Jan Neuman, NenoVision Brno; Olivier Thomas, Aix-Marseille University; Pawel Zieba, IMIM PAN Krakow; Ehrenfried Zschech, deepXscan Dresden.
- Round table discussion: Experiences from start-ups in materials characterization: Jan Neuman, NenoVision Brno; Robert Brückner, Senorics Dresden; Kristina Kutukova, deepXscan Dresden (Moderation: Ehrenfried Zschech, deepXscan Dresden).
- Tour on Wednesday morning: Gläserne Manufaktur Dresden, Lennéstr. 1, 01069 Dresden.

Program

Wednesday - 12.10.2022							
Begin	End	Duration		Name	Affiliation	Poster #	
13:00	13:15	0:15	Welcome	Ehrenfried Zschech	deepXscan		
13:15	14:15	1:00	Introduction about Correlative Materials Characterization – Concepts and examples	Jan Neuman Olivier Thomas Pawel Zieba Ehrenfried Zschech	NenoVision Aix-Marseille Univ. IMIM PAN deepXscan		
14:15	14:30	0:15	Coffee Break				
School of Young Scientist, Session 1 (Chair: Ehrenfried Zschech)							
14:30	14:45	0:15	Thermal stability and corrosion behaviour of biodegradable binary Zn alloys after plastic deformation	Magdalena Wróbel	IMIM PAN Krakow	#1	
14:45	15:00	0:15	Nano-XCT sub-microstructure of cementitious materials – influence of transport of ions and oxygen on corrosion of reinforcement	Anna Górska	AGH-UST Krakow	#2	
15:00	15:15	0:15	Three dimensional morphology comparison of the diatoms in both wet and dry states	Qiong Li	BTU Cottbus		
15:15	15:30	0:15	Thermomechanical Characterizations of Copper at Nanoscale by Laue Microdiffraction	Bassel Ayoub	STMICROELECTRONICS France	#3	
15:30	15:45	0:15	Development of novel THz EPR micro-spectroscopy technique	Martin Konečný	IPC Stuttgart/ CEITEC Brno	#4 (different titel)	
15:45	16:00	0:15	Coffee Break				
School of Young Scientist, Session 2 (Chair: Jan Neuman)							
16:00	16:15	0:15	Denoising images from similar patterns within them	Anil Kumar Mysore Badarinarayana	deepXscan / TU Dresden	#5	
16:15	16:30	0:15	Noise in sub-micron computed tomography data and its denoising	Marketa Tkadlecova	TU Brno	#6	
16:30	16:45	0:15	In-situ TEM study of mechanical failure on two-dimensional covalent organic framework	Bowen Zhang	Fraunhofer IKTS Dresden/ TU Dresden	#7	
16:45	17:00	0:15	In situ studies of the electromechanical effects of ZnO nanowires	Soufiane SAÏDI	Uni Aix-Marseille	#8	
17:00	17:15	0:15	In silico materials characterization: one step before synthesis	Dawid Falkowski	QSAR Lab Ltd	#9	
17:15	17:30	0:15	Coffee Break				
17:30	18:30	1:00	Round table discussions Moderation: Ehrenfried Zschech, deepXscan	Jan Neumann Robert Brückner Kristina Kutukova	NenoVision Senorics Dresden deepXscan		
19:30 Dinner							
Thursday - 13.10.2022							
Begin	End	Duration		Name	Affiliation	Poster #	
9:00	10:15	1:15	Invited introduction talk about Machine Learning in Materials Characterization	Florian Jug	Milano, Italy		
10:15	10:30	0:15	Coffee Break				
School of Young Scientist, Session 3 (Chair: Pawel Zieba)							
10:30	10:45	0:15	In situ micro X-ray diffraction of Ceria-doped zirconia micropillars during compression: a μ Laue investigation performed at BM32-ESRF synchrotron beamline	Marcelo Demetrio de Magalhaes	INSA Lyon	#10	
10:45	11:00	0:15	Mechanical properties during bending of magnetic shape memory Ni-Mn-Ga-based ribbons	Milena Kowalska	IMIM PAN Krakow	#11	
11:00	11:15	0:15	Electron Tractor Beam: Deterministic Manipulation of Liquid Droplets on Solid Surfaces	Iveta Ukropcová	BUT Brno	#12	
11:15	11:30	0:15	Micromechanical testing of the fracture behaviour of mollusks shells in dry and wet states	Stefan Weitz	Fraunhofer IKTS Dresden/ BTU Cottbus	#13	
11:30	11:45	0:15	Coffee Break				
School of Young Scientist, Session 4 (Chair: Olivier Thomas)							
11:45	12:00	0:15	How To Find Fossil Caries? Case Study Of A Tooth Of Plio-Pleistocene Dormouse	Pawel Bacal	ING PAN Warsaw	#14	
12:00	12:15	0:15	In-situ microscopy of catalytic oxidation of CO to CO ₂ on Pt surfaces	Karel Vařeka	CEITEC Brno	#15	
12:15	12:30	0:15	Impact of single and double-barreled structures on electrochemical performance of iron-titanium based anodes for sodium-ion batteries	Mikołaj Nowak	AGH Krakow	#16	
12:30	12:45	0:15	Effect of aging process on the superelasticity in Fe based SMA	Monika Czerny	IMIM PAN Krakow	#17	
12:45	13:00		Wrap-up				

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Abstracts
-Talks and Posters-

Thermal stability and corrosion behavior of biodegradable binary Zn alloys after plastic deformation

P1

Magdalena Wróbel^{1*}, Anna Jarzębska¹, Łukasz Maj¹, Paweł Petrzak¹, Mariusz Kulczyk²,
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Cardiovascular stents are one of those biomaterials, that do not need to be permanently placed at the site of implantation. The best solution is to use biodegradable materials. There are several possible candidates of the metals which could dissolve in physiological conditions. Among them, zinc seems to have a proper corrosion rate. However, pure zinc has poor mechanical properties and low recrystallization temperature and does not meet specific requirements for application as stents [1,2]. Nevertheless, plastic deformation, especially hydrostatic extrusion and alloying additives, for example, magnesium, can affect the microstructure, improving both parameters [3,4].

In the presented research, zinc-magnesium alloys with different magnesium addition (0.6 and 1.2 wt.% of Mg) were prepared by gravity casting, hot extrusion in 250°C (HE) and hydrostatic extrusion (HSE) in 4 passes. Thermal stability was tested by quasi-in-situ studies, in the temperature range from the human body to higher (above 100 degrees). To calculate the corrosion rate and observe the effect of the amount of the second phase on degradation behaviour, an immersion test for 7 and 14 days in Hanks' Balanced Salt Solution with controlled pH was performed. Mechanical properties were investigated using compression tests before and after 14 days of corrosion.

The microstructure of zinc-magnesium alloys consists of the α -Zn and intermetallic phase $Mg_{2}Zn_{11}$. After hydrostatic extrusion, grains were significantly refined due to the continuous dynamic recrystallization process (CDRX). Quasi-in-situ studies lead to the conclusion, that both alloys are thermally stable under 100°C. Moreover, above this temperature $Mg_{2}Zn_{11}$ phase delays the static recrystallization process. Immersion tests showed faster degradation of the $Mg_{2}Zn_{11}$ phase and the presence of corrosion pits in which mainly occurrence chlorine oxides. Mechanical properties after 14 days of immersion test did not visibly decrease.

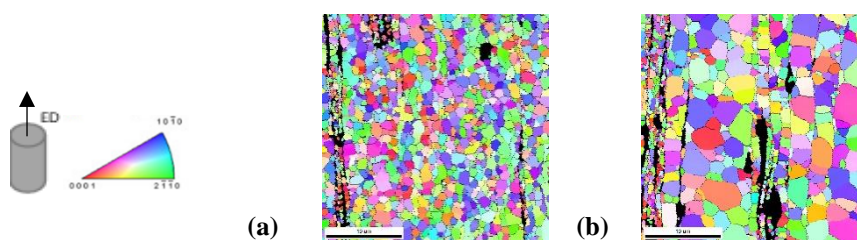


Figure 1. Zinc-magnesium alloy (a) after hydrostatic extrusion; (b) after annealing in 121°C

Acknowledgements

The research was financially supported by the National Science Centre Poland, project number UMO-2020/39/O/ST5/02692

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Nano-XCT sub-microstructure of cementitious materials – influence of transport of ions and oxygen on corrosion of reinforcement

P2

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Modern descriptions of concrete properties probe at the smallest length, but structural and chemical behavior are manifested at greater scales, thus nanoscale models must be integrated with macroscopic ones. Presented model is based on a real microstructure morphology where microscale geometry 3D is reconstructed from the nano-scale X-ray computed tomography data. Gel pores, capillary pores, and aggregates were segmented (Figure 1a) and 3D meshes were created (~2,300k tetrahedral elements) for numerical simulation using COMSOL Multiphysics®.

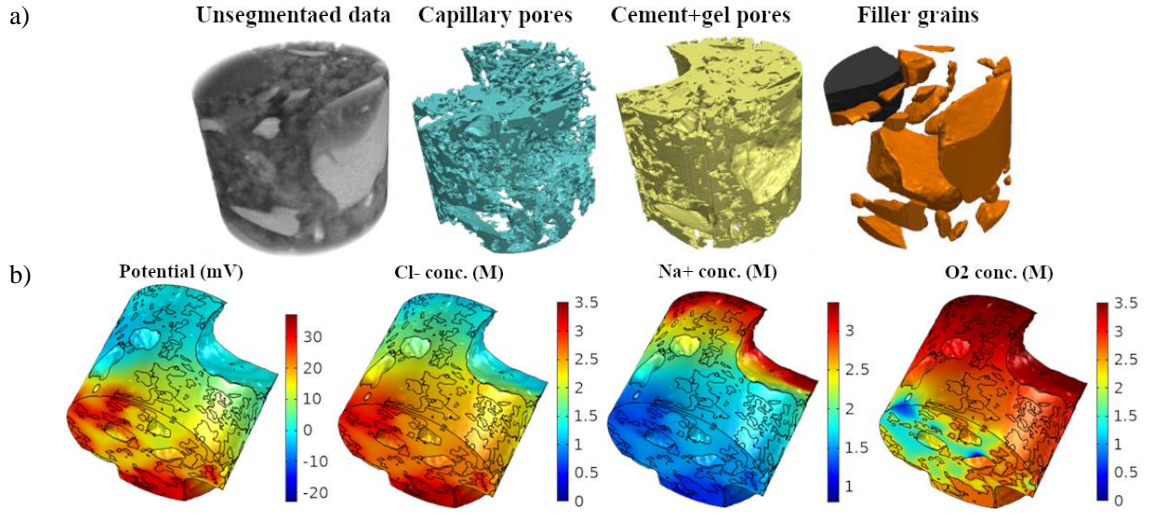


Figure 1. a) Unsegmented XCT data and results of phase segmentation; b) A 3D calculation of potential and concentration of species in real nano/micro structure for $t = 10$ s.

Transport of ions: Fe^{2+} , OH^- , Na^+ , Cl^- and O_2 in a sub-micro scale XCT-based geometry is governed by mass conservation law, Nernst–Planck fluxes, and embedded electroneutrality conditions (with Na^+ elimination). Appropriate material parameters are used for each phase. Equations for one phase are:

$$\sum_{i=\text{OH}^-, \text{Fe}^{2+}, \text{Cl}^-} \left(z_i - \frac{z_{\text{Na}^+} D_{\text{Na}^+}}{D_i} \right) \frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_{\text{Na}^+, \varphi} = R_{\text{Na}^+, \varphi}, \quad \frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i = R_i, \quad i = \text{OH}^-, \text{Cl}^-, \text{Fe}^{2+}, \text{O}_2$$

$$\mathbf{J}_{\text{Na}^+, \varphi} = -(z_{\text{OH}^-} - z_{\text{Na}^+}) D_{\text{Na}^+} \nabla c_{\text{OH}^-} - (z_{\text{Fe}^{2+}} - z_{\text{Na}^+}) D_{\text{Na}^+} \nabla c_{\text{Fe}^{2+}} - (z_{\text{Cl}^-} - z_{\text{Na}^+}) D_{\text{Cl}^-} \nabla c_{\text{Cl}^-}, \quad \mathbf{J}_i = -D_i (\nabla c_i + z_i \frac{F}{RT} c_i \nabla \varphi)$$

Tafel kinetics were assumed for boundary conditions, $i_k = i_k^0 \cdot \exp\left(\pm \frac{\alpha_k F}{RT} (U_{\text{rebar}} - \varphi - E_{\text{eq},k})\right)$. Exemplary

distributions of electrical potential and concentrations of ions and oxygen in a sample with real microstructure are presented in Figure 1. The model shows that description involving real micro-morphology of concrete coupled with transport of multi-ion system and charge transfer reactions on the rebar surfaces is feasible using modern equipment and computational tools. It allows a full description of current, potential and species distribution, thus paving a way for the predictive diagnosis of rebar corrosion. Comparison with simplified models as well as 3D vs. 2D computations are presented.

Acknowledgments.

This research was supported by the National Science Centre, Poland, grant No. 2020/37/B/ST8/02805.

Three-dimensional morphology comparison of the diatoms in both wet and dry states

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Diatom is the single eukaryotic algae cell abundant in nature with the silica cell wall named frustule. As one of the very interesting microorganisms for research on different disciplines and applications, such as material design, biotechnology, biofouling, they are widely studied and regarded as one of the promising biological materials due to their excellent physical and chemical properties. How to imaging the diatoms three dimensionally (3D) remains a great challenge. During the study, the 3D morphology of diatom frustules from centric to pennate diatom frustules are investigated by nano-XCT. A critical progress is that we design a sample holder in nano-XCT to make the imaging of the diatoms in wet state possible without too much sample preparation. The 3D imaging by nano-XCT successfully shows the inner organelles and the silica cell wall structures. Furthermore, there are great differences between the morphology and volume of the same diatom in both wet and dry states. This work provides significant discovery in the morphology of the diatom frustules and diatom cells and the methodology development in the nano-XCT system could be used as a route for the study of diatoms in the future.

Acknowledgments

Thanks a lot to Dr. Jürgen Gluch (now: Robert Bosch Semiconductor Manufacturing Dresden GmbH), and to the former colleagues from Fraunhofer Institute of Ceramic Technologies and Systems IKTS: Dr. Birgit Jost, Dr. Juliane Posseckardt, Dr. Zhongquan Liao, Dr. André Clausner for the discussion and support during the PhD study.

The authors also acknowledge Prof. Andrzej Witkowski from University of Szczecin, Poland for supplying the diatom species and Dr. Izabela Zgłobicka from Białystok University of Technology for using FIB/SEM imaging the *D. Gaminata*.

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Thermomechanical Characterizations of Copper at Nanoscale by Laue Microdiffraction

P3

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Copper is the main metal for interconnects in integrated circuits (ICs). Its material properties greatly change with the reduction of interconnect sizes (micro to nanoscale) used in ICs due to its microstructure evolution. Cu is also known to be elastically highly anisotropic with a higher Young's modulus along the [111] orientation which explains the clear relation reported between the micrometric Cu grain orientation and yield strength [1]. In addition, a modified plastic behaviour was put in evidence for nanocrystalline Cu [2]. However, the thermo-mechanical properties dependence on orientation is still unsolved for Cu crystals with a size ranging between 100 to 1000 nm. This is of paramount interest for 3D stacking technologies requiring Cu-Cu bonding [3-4]. To target this, in-situ white beam Laue microdiffraction temperature-dependent measurements (up to 400   C) were performed on samples with Cu pads width ranging from 3   m to 300 nm (Fig. 1(a)) at the BM32 beamline of the ESRF (Grenoble, France). The analysis of the Laue microdiffraction patterns, using the LaueTools software, gives access to the microstructure and deviatoric strain with a very high resolution down to 10⁻⁴ [5]. Orientation maps, shown in Fig. 1(b), clearly evidence a decrease in the grain number with reducing width, from 7 grains on average for the 3   m pad to a single grain for the 300 nm Cu pad. The orientation remains unchanged with temperature up to 400   C whatever the grain size. For grains with orientation close to [001], shown in Fig. 1(c), the 300 nm monocrystalline grain exhibits much larger deviatoric deformation at temperature above 350   C than the 3   m grain. For the 300 nm Cu grains, 3D FEM is done to fit the experimental results with a Ludwick power model to evidence any plastic behaviour. The results indicate a plastic deformation only for grain with orientation close to [001] and a yield strength σ_y that increases when orientation approaches [111] [6]. In addition, the total deformation is found dependent on the orientation with higher deformation toward [001]. This allows better control of Cu-Cu bonding with decreasing Cu pad width.

Acknowledgments

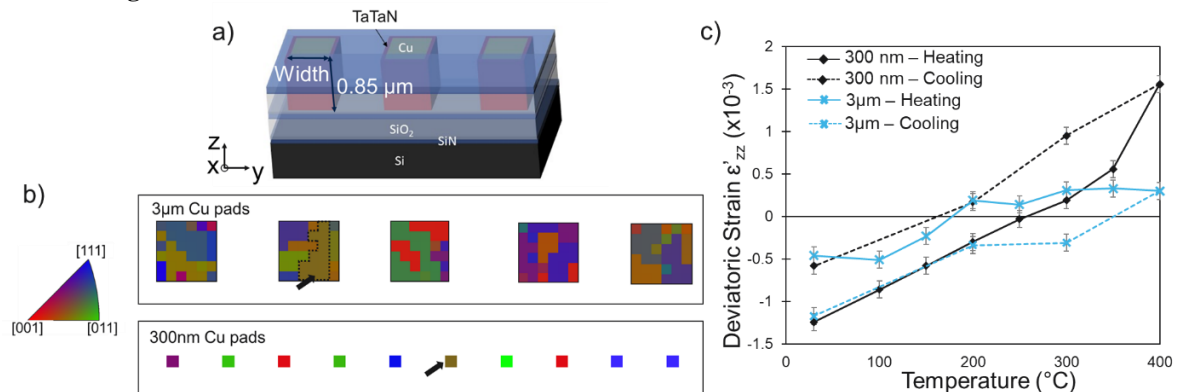


Figure 1. a) Schematic illustration of the sample used for study, b) Inverse Pole Figure (IPF) orientation map perpendicular to the Cu pad surface for the 3   m (top) and 300 nm (bottom) Cu pads and c) deviatoric strain evolution with temperature for two grains of orientation close to [001] selected between the 3   m and 300 nm Cu pads (black arrows in (b)).

We acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation facilities, and we would like to thank Jean-Sebastien Micha and Samuel Tardif for assistance in using beamline 32. This work was supported by the French National Research Agency (ANR) under the "Investissements d'avenir" programs: ANR 10-AIRT-0005 (IRT NANO-ELEC) and by the cooperative Research & Development program "IPCEI, Nano 2022".

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Development of novel THz EPR micro-spectroscopy technique

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In the field of chemistry, physics and biology the electron paramagnetic resonance (EPR) spectroscopy is an essential technique for investigation of paramagnetic compounds such as organic and inorganic radicals and transition metal or lanthanide complexes [1]. However, EPR spectroscopy is typically limited to the characterization across the whole volume of studied sample and does not provide any information about the variation of properties along the sample surface. Here, we report on the development of novel technique combining the high frequency (250–360 GHz), high field (0–12 T), low temperature (2–300 K) electron paramagnetic resonance spectroscopy and scanning probe microscopy. The working principle of this unique technique is based on plasmonic-based magnetic field enhancement in the vicinity of the SPM probe with the plasmonic antenna over the tip apex [2]. Thanks to this approach, it is in principle possible to reach a sub-diffraction-limited spatial resolution down to 1 μm . This allows to map spin electronic properties of the sample together with surface morphology.

Acknowledgments

This research has been supported by European Union's Horizon 2020 programme FET-OPEN project PETER, GA 767 227. The Center for Integrated Quantum Science and Technology (IQST), and the Carl Zeiss Foundation are also acknowledged. The authors thank Brno University of Technology (FSI-S-20-6485) and the GACR project 20–28573S. The authors acknowledge financial support from the Spanish Ministry of Science, Innovation and Universities (national project RTI2018-094830-B-100 and the project MDM-2016-0618 of the Maria de Maeztu Units of Excellence Program) and the Basque Government (grant No. IT1164-19).

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KPFM in SEM - Simultaneous Kelvin Probe Force Microscopy and Scanning Electron Microscopy

P4

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With the introduction of Atomic Force Microscope (AFM) to the Scanning Electron Microscope (SEM), some yet unexplored ways of sample characterization open up. Kelvin Probe Force Microscopy (KPFM) is an AFM-based technique for measuring surface electrical properties in nanoscale [1], which can measure local surface potential or visualize trapped charge, for example. The simultaneous combination of KPFM and SEM imaging provides a new direct view on the problematic of interaction between electron beam and the sample.

To our knowledge, there is no published study about simultaneous KPFM and SEM imaging. We use small and compact NenoVision LiteScope AFM that can be inserted into various SEM chambers [2]. In this poster, we present our first advances in this topic, focusing on basic principles of operation and data interpretation. Furthermore, we would like to also discuss other potential applications of the technique.

Acknowledgments

This work was supported by Technological Agency of the Czech Republic (TJ01000434). CzechNanoLab project LM2018110 funded by MEYS CR is gratefully acknowledged for the financial support of the measurements/sample fabrication at CEITEC Nano Research Infrastructure.

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In X-ray and electron microscopy, obtaining noise-free images of biological samples or delicate materials is often difficult because of the limitation on the amount of *dose* that can be used. Therefore, image denoising is essential for the analysis of such noisy images. State of the art image denoising methods are dominated by supervised Convolutional Neural Network (CNN) based methods. However, if noise-free ground truth images are unavailable, supervised CNNs cannot be used. To address this problem, a denoising algorithm is proposed that uses similar patterns within images for denoising [1]. The proposed method does not require noise-free images for the denoising task. It is based on the concept that averaging images with a same signal and independent noise, suppresses the overall noise [4].

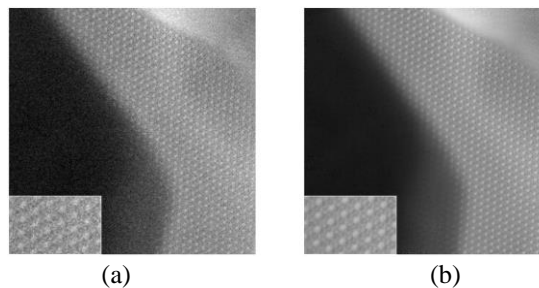


Fig 1. Noisy image (a) and it's denoised version (b) obtained by applying the proposed method

The proposed method uses *normalized cross correlation* to form groups of similar patches within images. Then clustering methods are applied to form subgroups within these groups. The centroids obtained from clustering are back plotted to the locations of the members of the cluster. During back plotting, a gaussian mask is used to suppress the pixels at the edges of the centroids. This ensures that the denoised result is seamless. An example of the denoising result is shown in Fig 1. To optimize the runtime performance, GPU computation is made possible. Further, variance map is developed for the evaluation of denoised results.

The proposed method is compared with other successful denoising methods [2][3][5] that do not require a noise free image. The results of proposed algorithm show promise in denoising images, especially those that have similar regions within them. The proposed method is also extended to use multi-modal images, where information from different modes is shared for the denoising process.

Acknowledgments

Dr. Florian Jug (Human Technopole, Milan, Italy), Amadeus Samuel Tragl (Fritz Haber Institute, Berlin, Germany), Prof. Dr. Ehrenfried Zschech (deepXscan GmbH, Dresden, Germany) and Prof. Dr. Gerd Schneider (HZB, Berlin, Germany).

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X-ray imaging and X-ray computed tomography (CT) recently became very important and highly successful non-destructive diagnostic tools in many fields – from medicine to material sciences, and the demand to produce images with higher spatial resolution and better perceptual quality is still increasing. But due to the complexity of the entire CT data acquisition process, the noise in projection images is inevitable [1]. This noise can significantly distort acquired information and downgrade the perceptual quality of reconstructed images and their interpretation. Hence, to provide high-resolution computed tomography images, some methods to reduce noise should be included in the CT process. To this date, many papers have been focused on noise reduction in CT data, but mainly in connection with low-dose medical CT, and there is little known about the properties of noise in submicron CT and its suppression. In this ongoing project, the focus is on datasets from a lab-based CT system (Rigaku nano3DX system) with submicron resolution equipped with a CCD detector. The first step to finding a complex denoising methodology is to determine the distribution and model of the noise present in the projection images. In the literature, this noise is widely assumed to be additive-white-Gaussian (AWGN) with constant variance [2], but results show that a signal-dependent noise model is more suitable for acquired data. The exact parameters of the noise model in the projection domain were established using bright field images taken with different exposure times. This noise model was used to simulate noise in test images, and multiple denoising algorithms, both for 2D images and for volumetric datasets, were tested on these images. Simple filters as well as more sophisticated and robust denoising methods were included in the testing. These algorithms were evaluated using different approaches. The full reference metrics peak-signal-to-noise-ratio (PSNR), structural similarity index (SSIM), and mean squared error (MSE) were used to compare algorithms quantitatively. Discussion of all selected algorithms' executional time, edge and texture preserving, but especially spatial resolution preserving, using projection images of the JIMA resolution chart has been done.

Acknowledgments

This research was carried out under the support of CEITEC computed-tomography laboratory.

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***In-situ* TEM study of mechanical failure on two-dimensional covalent organic framework**

P7

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Two-dimensional covalent organic frameworks (2D COFs) are an emerging class of 2D crystalline polymers, which are the covalently linked networks of monomers along orthogonal directions [1], and has growing attention for electronics/optoelectronics, energy storage/conversion, gas separation, catalyst applications because of their designable structures and multifunctional properties [2-5]. However, although they are proved to possess outstanding mechanical properties and envisioned to be core parts in nanodevice, particularly flexible device [6-8], revealing the fracture behaviour and mechanism of 2D COFs at molecular level has not been realised yet, which is crucial to tailor their mechanical properties for improving mechanical reliability of nanodevice. To this end, we demonstrate an *in-situ* fracture process of an imine-based 2D COFs in transmission electron microscopy (TEM, Libra200, Carl Zeiss). By optimizing the transferring and patterning procedures, we report that under tensile stress, a large elastic strain up to ~4.9% is achieved in 2D COFs, with corresponding elastic modulus of ~7 GPa. Furthermore, the pathways of crack propagation are not sharp with some bifurcations along the crack edges, and both the intergranular and trans-granular fracture, as well as the delamination, are clearly visible. Our *in-situ* experimental investigations can be furtherly elucidated by molecular dynamic simulation, which is able to provide in-depth insights into intrinsic fracture mechanisms of 2D COFs and pave the way for future flexible electronic applications.

Acknowledgments

Bowen Zhang acknowledges the financial support from China Scholarship Council (CSC). The authors also thank the technical support from J. Posseckardt and S. Conzendorf from Fraunhofer IKTS for SEM and FIB operation, and Z. Wang and J. Zhang from the Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, for sample preparation and transferring.

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Piezoelectric semiconductor nanowires (NWs) have been researched as building blocks for various energy transducing applications including mechanical energy harvesting [1,2], sensors [3] and piezotronic devices [4]. The electromechanical interaction, also known as piezoelectricity, couples the mechanical and the electrical state in crystalline materials with no inversion symmetry, *i.e.*, the application of mechanical strain results in the generation of electrical charge and vice versa. The effective piezoelectric coefficient was suggested to increase with decreasing NW diameter due to finite size effects, thus increasing the conversion efficiency of mechanical into electrical energy and back making NWs promising candidates for future mechanical energy transducers.

The measurement of the piezoelectric response of individual nanostructures by classical methods like piezoelectric force microscopy is highly challenging because of the presence of many artefacts like electrostatics. On the other hand, X-ray diffraction is highly sensitive to strain making it ideal to study the deformation of electrically actuated piezoelectric nano-objects. In addition, synchrotron X-ray beams are nowadays routinely focused down to few hundred nanometers allowing for studying individual nanostructures.

Here, we report on *in-situ* Laue microdiffraction studies of the piezoelectric response of individual ZnO NWs actuated electrically. Zinc oxide NWs were grown by a hydrothermal process on Si substrates. The ZnO NWs were detached from their growth substrate and dispersed on a Si wafer where individual NWs were contacted electrically using lithography methods. Laue microdiffraction was performed at the BM32 beamline at ESRF in Grenoble where the incident polychromatic X-ray beam was focused down to 300 x 500 nm² using a pair of Kirkpatrick-Baez mirrors. Laue microdiffraction patterns were recorded using a sCMOS PhotonScience detector. During the application of electric voltages to the ZnO NWs, Laue peaks are displaced on the detector (Fig. 1(a)). The diffraction patterns were indexed using the LaueTools software providing access to the orientation of the crystals as a function of the applied voltage and, thus the rotation of the crystal (Fig. 1(b)).

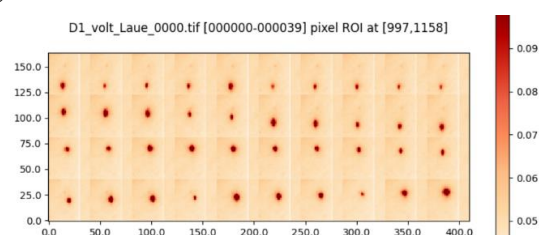


Fig. 1(a) Laue peak movement of a ZnO nanowire

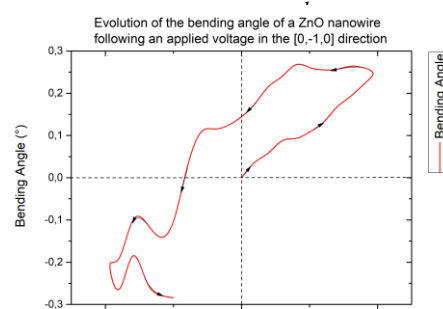


Fig. 2(b) Crystal rotation during the application of a current

Acknowledgments

We would like to thank the funding provided by the ANR within the framework LATINO (ANR-21-CE50-0026-03) as well as the ESRF and SOLEIL synchrotron facilities for the allocated beamtimes.

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The well-organized doped - or modified- TiO₂-based nanotubes (NTs) have been widely designed as highly promising photocatalysts for degradation of pollutants, H₂ production, or photoconversion of CO₂ [1-3]. The main limitation in designing sustainable and advanced TiO₂-based materials is thousands of possible combinations of structural features and a lack of systematic knowledge about the relationship between experimental conditions, structure modification, and the efficiency of newly designed TiO₂ nanotubes. Because of the high cost and time-consuming experimental study, it is irrational to synthesize and test all possible structures to find the most optimal combination. [1-3] Thus, in our research, for the first time, we applied machine learning (ML) methods combined with a high throughput screening methodology to study the quantitative relationship between the experimental condition, structure modification, and the efficiency of newly designed well-organized TiO₂ nanotubes. The data-driven approach has been utilized based on a developed library of available literature data of ordered TiO₂ NTs synthesized in thin layers synthesized by anodic oxidation of titanium foil that is highly active under vis or UV-Vis light. Then, by employing Hierarchical Clustering analysis (HCA) and Principle Component Analysis (PCA), we grouped and examined the structural similarity of 144 different TiO₂-based NTs. Then, we have developed a predictive Quantitative Structure-Property Relationship model (QSPR) for the photocatalytic activity of investigated TiO₂-based nanotubes NTs. Finally, through proposed supervised learning methods and developed predictive models, we have determined how to manipulate structural features and experimental conditions to reduce cost and speed up the process of efficient product design at the earliest possible stage. The proposed data-driven approach may be extended to optimize the design process of another type of advanced multicomponent nanomaterials in line with the sustainability-by-design strategy.

Acknowledgments

The study was conducted under funding that has been received from the European Union's Horizon 2020 research and innovation programme via NanoInformaTIX Project no. 814426 and DIAGONAL Project no. 953152.

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In situ micro X-ray diffraction of Ceria-doped zirconia micropillars during compression: a μ Laue investigation performed at BM32-ESRF synchrotron beamline

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In recent years, zirconia ceramics have been widely used in dentistry as ceramic implants because of their unique structural properties, combined with their great aesthetics and biocompatibility. Their notable structural properties arise from a displacive martensitic transformation (tetragonal \rightarrow monoclinic), which produces compressive stresses around the transformed regions that in turn increase the fracture toughness (K_{IC}). In this sense, ceria-doped zirconia ceramics have attracted increasing attention due to their resistance to Low-Temperature-Degradation (LTD) and their high fracture toughness (K_{IC} , 7-16 MPa·m^{1/2}). Still, the applicability of this novel ceramic needs further research to fully comprehend its mechanical properties and how the transformation occurs. To that end, characterization at the micro/nanoscale is of interest.

With that in mind, our work focuses on understanding the tetragonal (metastable) \rightarrow monoclinic phase transformation in single crystal micropillars using in situ Laue microdiffraction (μ Laue diffraction) during compression tests. First, 12 mol% ceria-doped tetragonal zirconia ceramics were prepared by cold isostatic pressing followed by sintering in air at 1600°C for 10h dwell time, aiming to obtain a grain size of the order of \sim 8 μ m, large enough for milling a single-crystal micropillar within a single grain. Micropillars with a diameter of 0.5 to 0.7 μ m and a height of 2.2 to 3.3 μ m were milled by focused ion beam out of the bulk material in specific directions previously indexed by electron backscatter diffraction. These micropillars were compressed in situ at the BM32-ESRF beamline using a nanoindenter FT-NMT04 equipped with a diamond flat punch. The micropillar deformation was followed by μ Laue diffraction. The latter allows monitoring of the orientation and crystalline structure of the specimen during the mechanical test, as well as determining the deviatoric elastic strain and the shape of diffraction peaks, which is related to the plastic activity.

A preliminary analysis of the data will be presented. We will discuss the potential effect of imperfections of the micromechanical test (e.g. misalignment) as well as the influence of the crystal orientation. These first measurements will serve as a benchmark for more complex mechanical tests in particular on bi-crystals.

Acknowledgments

We would like to thank the funding provided by the ANR (NANOTRIP project: ANR-21-CE08-0019-02) and the ESRF facility for the beam time.

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Mechanical properties during bending of magnetic shape memory Ni-Mn-Ga-based ribbons

P11

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Mechanical properties of magnetic shape memory Ni-Mn-Ga-Co-Cu melt-spun ribbons during bending tests were studied. Different mechanical characteristics were obtained depending on the loading direction with respect to the ribbon's side. Higher values of maximum bending force was observed in the case of the so-called "free side" (FS), which didn't directly contact the rotating copper wheel as is the case of the "wheel side" (WS).

Effect of annealing temperature was also examined during cyclic bending experiments. For this purpose, as-melted ribbons were selected and divided into five groups and then annealed at 373 K, 573 K, 773 K, 973 K and 1173 K for 30 minutes. Each bending test was performed in 10 cycles. It was shown that annealing at 773 K causes an increase of the maximum bending force, which is a result of atomic ordering of the crystal lattice. On the other hand, the bending force decreases upon annealing at 1173 K, which can be explained by recrystallization process. Mechanical response of the ribbons annealed at different temperatures was observed and correlated with their microstructure changes. EBSD measurements showed that significant grain growth occurs in the ribbons microstructure after annealing at 1173 K for 30 minutes.

Martensitic transformation temperature (M_s) was determined using differential scanning calorimetry (DSC) method for as-melted and annealed ribbons. The highest value of M_s was detected in the case of the ribbons annealed at 1173 K, which was affected by grain growth due to recrystallization.

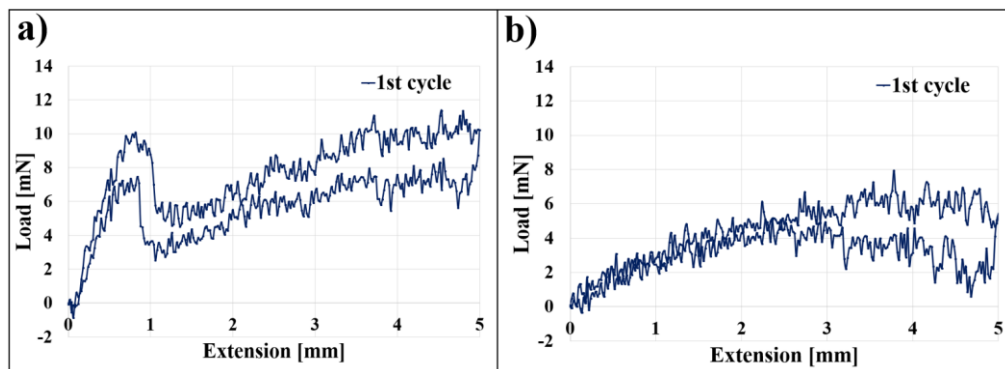


Figure 1. Mechanical characteristics recorded during first cycle of bending tests of Ni-Mn-Ga-Co-Cu melt-spun ribbons with the load applied to the free side (a) and wheel side (b).

Acknowledgments

The work carried out within the grant nr 2020/39/O/ST8/01343 financed by the National Science Centre of Poland.

Electron Tractor Beam: Deterministic Manipulation of Liquid Droplets on Solid Surfaces

P12

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Motion of liquid droplets is studied across many subfields of physics and manipulation of nanoscale droplets on demand holds great promise in e.g., nanotechnology [1, 2]. Spontaneously moving droplets have been observed in many systems and efforts are being made to control the movement of the droplets [3–6]. We show that AuGe droplets on germanium substrate can be manipulated by an electron beam in electron scanning microscope (SEM).

The electron beam is locally heating the substrate and thus inducing a temperature difference in the vicinity of the focused point. A droplet located along this temperature difference is heated unequally. If the difference of temperatures on opposite sides of the droplet is high enough, it causes the droplet to move toward the warmer area, i.e., against the electron beam. We have demonstrated manipulation of droplets larger than 400 nm, as the smaller droplets are difficult to move, probably due to insufficient temperature difference across the small droplet. Droplets larger than 5 μm often move spontaneously without the electron beam control.

To quantitatively analyze this phenomenon and to reveal the mechanism behind, experimental observations under different conditions (beam current, sample temperature, scanning strategy) and simulations were combined. The obtained insights suggest that the temperature gradient in substrate causes a concentration gradient in droplets, which yields in *dissolution-diffusion-deposition* flow [7] of Ge atoms through the droplet (See Figure 1). Results also suggest that the motion is limited by the dissolution of the substrate below the droplet.

Bearing in mind that the liquid droplets are utilized in many fields of nanotechnology, the possibility to precisely navigate the droplet to a predetermined location is an attractive technique for e.g., positioning of droplets for nanowire growth, on-surface synthesis or device prototyping.

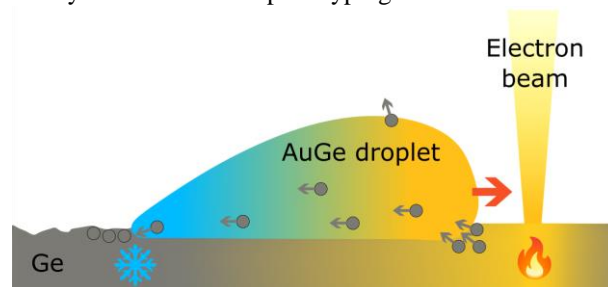


Figure 1. AuGe droplet on Ge substrate with temperature gradient, which is caused by heating from electron beam. On the warmer, Ge solubility is increased, thus Ge atoms (gray circles) are absorbed from substrate. Inside the droplet, the Ge atoms diffuse, and they are deposited on the colder side. In consequence, the droplet is moving toward the warmer area, i.e., the droplet is following the electron beam.

Acknowledgments

CzechNanoLab project LM2018110 funded by MEYS CR is gratefully acknowledged for the financial support at CEITEC Nano Research Infrastructure. The research was supported by Technological Agency of the Czech Republic (FW01010183) and by Fund of Science (FV22-18) of Brno University of Technology.

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Micromechanical testing of the fracture behaviour of mollusks shells in dry and wet states

P13

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Housings of mollusks shells can withstand great stress without breaking. Understanding this remarkable material behavior and using this knowledge to design bio-inspired engineered materials will open new pathways in material science. In this work, micro indentation experiments are reported and crack propagation in dry and wet shells specimens is discussed.

Recent studies [1] have shown that the toughness behavior of mollusks shells greatly depends on the orientation of the prismatic layer. The structure withstands a much higher compressive stress when the force is applied in the direction of the prisms rather than when the load is exerted perpendicularly to them. In further tests, two different cracking mechanisms were observed [2]. While loading the structure in the direction of the prisms resulted in crack propagation towards the organic part, where the cracks are stopped, the second case revealed no crack stopping, but a catastrophic failure of the sample structure, as illustrated in Fig. 1.

The work includes a subsequent analysis of the two fracture experiments on *P. margaritifera* shells. Microindentation tests are carried out to compare the fracture experiments for dry and wet environments. Furthermore, the effect of fatigue loading on shells is analyzed by applying a dynamical sinusoidal load function with the indenter. Results are visualized using an X-ray microscope utilizing a photon energy of 8keV.

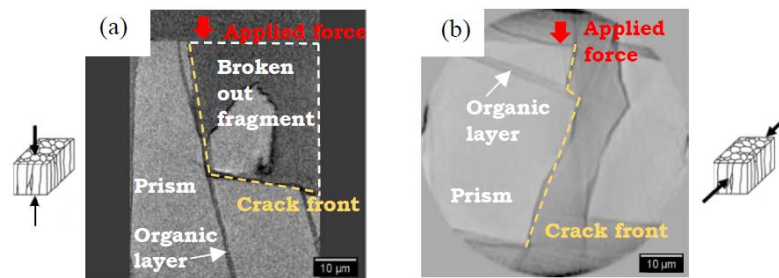


Figure 1. Radiographs of *P. margaritifera* shells after microindentation: (a) Crack stopped by the organic layer; (b) Catastrophic failure of the structure [2]. Description; (b) Description.

Acknowledgments

The authors thank Kristina Kutukova and Martyna Strag for their previous work and insights which have supported the overall work.

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How To Find Fossil Caries? Case Study Of A Tooth Of Plio-Pleistocene Dormouse

P14

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The dental infections are thought to have been widely occurring in vertebrates since the Paleozoic era (from over 500 Mya) [1, 2]. Despite that, only few pre-Holocene (up to ca. 12 000 years ago) fossil examples of bacteria-related tooth decay have been described in the scientific literature so far.

Although some associations between bacteria and their host species do occur in the fossil record [e.g., 3], the clear proof of an association between a pathological condition and the microbial pathogen responsible for its development was missing. To our knowledge this is the first report of such case.

We discovered a fossilized bacterial microflora preserved *in situ*, which is associated with enamel demineralization and dentine inflammation within an isolated tooth of the Plio-Pleistocene (period lasting c.a. Mya, to c.a. 12 thousand years ago) dormouse *Glis sackdillingensis* (Rodentia, Gliridae, depicted a Fig.1. left bottom corner inset). The specimen was recovered from the fossiliferous *terra rossa* sediments, and the age was dated at the Late Pliocene (2.9–2.6 Mya) [4,5].

A routine SEM examination of dental *Glis* specimens with the intention of studying enamel microstructure fossilized bacteria was conducted. To expose enamel structure teeth were embedded in epoxy resin, polished perpendicularly to the vertical axis and treated with dilute orthophosphoric acid for ca. 60 seconds.

During examinations we found peculiar structure of unknown origin in part of labial-side enamel of one of the samples. It appeared as irregularly shaped, black, void space (Fig.1.A, B). Since we suspected that we may have a rare example of caries related tooth decay we deepened our investigation using combination of various techniques such as: SEM, EDS, micro tomography, X-ray photography and visible light microscopy. Correlation of data allowed us to prove that this structure is actual caries. Moreover, we were able to observe bacteria traces in the sample (Fig.1. D,E,F). Those were detected during a SEM examination only in combination of certain conditions such as: thin or no conductive layer and low as possible both tension and current of the SEM beam.

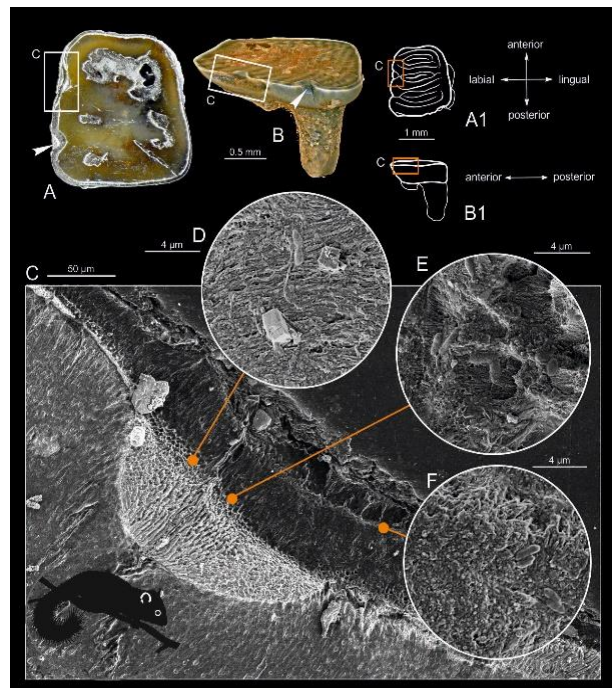


Figure 1. (A) The overview of tooth. The cavity area is highlighted. (B) 3D CT model of tooth. (C) A SEM picture of the cavity area with the damage to the enamel and the dentin layers visible. (D, E, F) A compilation of SEM photographs showing bacterial fossils found in tooth. Inset in left bottom corner is a schematic silhouette of *Glis sackdillingensis*.

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Exhaust gases released into the atmosphere by global industrialisation constitute a significant contributor to deterioration of the environment. CO arises from the incomplete combustion of fossil fuels and is a domain feature in the development of alternative fuels. As an unwanted by-product during the production of methanol in CO₂ hydrogenation, excessive CO feeds to hydrogen fuel cells may cause decay in their electro-generation performance [1]. Therefore, the development of efficient catalytic processes with high CO conversion rates is essential for the modernisation of our industry sectors and the minimisation of waste production as a result of a circular economy.

Catalysis is a process that increases the rate of a reaction by lowering the activation barrier. Although, throughout the reaction, the catalyst remains undepleted, in the long term, the surface can exhibit sintering, faceting, or poisoning that lead to the catalytic activity lowering [2]. Conventionally, heterogeneous catalysis experiments are carried out by ex-situ high- vacuum microscopy techniques to determine the effect of ambient atmospheres on a catalyst. Nevertheless, to avoid atmospheric contamination and to directly correlate surface processes with external influences (pressure, temperature), the real-time in-situ characterisation of surface and on-surface dynamics is of particular interest for catalysis research.

The kinetics of the adsorption and diffusion mechanisms of gas-phase and temperature- induced processes during CO oxidation give rise to spatial- and temporal-dependent behaviour on polycrystalline platinum surfaces. Many conventional surface science techniques may be adapted, yet not all offer sufficient chemical, spatial, and temporal resolution. In our group, we employed state-of-the-art UHV in-situ scanning electron microscope (SEM) and in-situ static secondary ion mass spectrometry (SSIMS) for real-time observations. Correlative approach is carried out to compare the chemical composition of the surface layers (SSIMS) with the changes in the work function (SEM) with the mass spectrometer gas flow data. In addition, we employed atomic force microscopy (AFM) capable of in-situ measurements within the microscope chamber. The correlative probe electron imaging is set to reveal a connection between self-promoting wave behaviour and the surface-active sites as any facets boundaries are visible in the AFM topography. We aspire to investigate the tip-sample interaction of oscillating adsorbed gases during several AFM modes.

Acknowledgments

We acknowledge CzechNanoLab Research Infrastructure supported by MEYS CR (LM2018110).

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Impact of single and double-barreled structures on electrochemical performance of iron-titanium based anodes for sodium-ion batteries

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Due to the tremendous growth of the electric vehicle industry and demand for Li-ion batteries we may soon face a shortage of production capability [1]. In the same time we observe spiking prices of crucial elements for Li-ion batteries such as lithium, graphite, nickel and cobalt. For this reasons, in the last few years Na-ion technology has emerged as one of the most promising technologies to Li-ion as it may offer competitive ratio of stored energy to battery production cost. Our work refers to development of proper anode materials and focuses on investigation of crystal structure and electrochemical properties of iron-titanium based oxides that react with sodium according to intercalation mechanism. Here we show possible application of single and double-barreled NaFeTiO₄, Na_{0.9}Fe_{0.9}Ti_{1.1}O₄ and Na_{0.8}Fe_{0.8}Ti_{1.2}O₄ as an anodes in Na-ion batteries.

NaFeTiO₄, Na_{0.9}Fe_{0.9}Ti_{1.1}O₄ and Na_{0.8}Fe_{0.8}Ti_{1.2}O₄ oxides were obtained in two routes [2]: 1) citrate assisted sol-gel method, where the samples were fired at 700°C for 6h or 900°C for 4h and 2) solid-state high-temperature reaction where samples were fired at 900°C for 20h. Structure, composition and morphology were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen absorption isotherms. Electrical conductivity was calculated in impedance spectroscopy (IS) measurements and electronic-band gap was estimated from UV-VIS spectra. Electrochemical performance in CR2032 coin cells was investigated in galvanostatic discharging/charging experiments in various temperatures. Three different electrolytes were examined to improve coulombic efficiencies. Mossbauer spectroscopy spectra and XAS spectra were collected to investigate mechanism of reaction.

The sol-gel route yields materials that possess diminished grain size and better morphology compared to samples prepared via high-temperature solid-state route. Impedance spectroscopy measurements showed that total electric conductivity of double-barreled structures is one order of magnitude higher than single-barreled while the lowest activation energy is reported as 0.82 eV for Na_{0.8}Fe_{0.8}Ti_{1.2}O₄ and 0.86 eV for NaFeTiO₄. Discharging/charging experiments under various current loads indicated that Na_{0.8}Fe_{0.8}Ti_{1.2}O₄ has the highest capacity of about 150 mAh g⁻¹ (after 30 cycles, C/20) with the mid-point voltage of 1.3 V vs metallic sodium. Replacement of conventional electrolyte NaPF₆ in EC:PC for NaPF₆ in diglyme resulted in: (1) increasement of coulombic efficiency in the first cycle, (2) higher capacities under high currents, (3) lower charge transfer resistance. Ex-situ experiments of electrodes after discharge as well as one full cycle revealed minor changes of unit cell parameters. Experiments in temperatures from -20°C to 60 °C showed that Na_{0.8}Fe_{0.8}Ti_{1.2}O₄ can preserve a large fraction of its initial capacity: 70 mAh g⁻¹ at -20°C and 177 mAh g⁻¹ at 60°C. Also such measurements showed that beside Fe³⁺/Fe²⁺ redox pair, the Ti⁴⁺/Ti³⁺ may be also involved in the electrochemical reaction.

Acknowledgments

This work was supported by the Polish Ministry of Science and Higher Education (MNiSW) under grant number 0046/DIA/2017/46

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Over the last decades, there has been increasing interest in the new shape-memory alloys SMAs exhibiting shape memory effect SME [1]. SME is a phenomenon, in which a material has the ability to return to its original size and shape when heating above a certain characteristic transformation temperature [2]. This kind of effect is due to a diffusionless, reversible, thermoelastic martensitic transformation, which can be induced by either change in temperature, stress, pressure, or magnetic field [3]. All other related properties such as two-way SME, superelasticity, rubberlike behavior, and damping capacity also have their origin in this transformation. These unique material behaviors are of great interest in industrial and technological applications where strain recovery is at the core of the design process.

Superelasticity is an isotherm process where the phase transformation from austenite to martensite phase occurs under an external load, Fig. 1. Since, the martensite phase is unstable, after unloading it transforms again to the austenite phase. Any SMA that shows superelasticity can also exhibit SME as well, however it involves heating and cooling cycles. In other words, the obtained martensite is stress-induced, and it goes back to austenite after the stress release producing a stress-strain loop with a hysteresis [4].

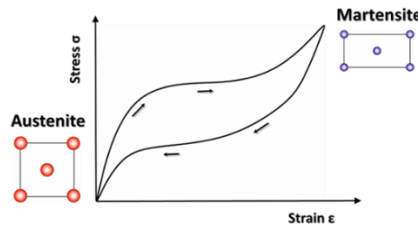


Figure 1. Schematic illustration representing superelastic effect.

In order to obtain role of crystallographic texture in multicomponent Fe- based shape memory alloys (containing Ni, Co, Al, Ta, Nb, Ti) was studied. The polycrystalline material was investigated after application of HE (hydrostatic extrusion) processing. In order to design functional polycrystalline materials, the interactions of twin boundaries and grain boundaries have to be understood [5]. Therefore, hydrostatic extrusion way of introducing those boundaries was used [6]. The microstructure after hydrostatic extrusion was analysed with Synchrotron X- ray diffraction, Transmission Electron Microscopy and Scanning Electron Microscope.

Acknowledgments

Acknowledges the financial support of the National Science Centre of Poland through project 2020/37/N/ST5/03134

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