



9th European Nanoanalysis Symposium

"Nano-scale materials characterization - Advances in data acquisition and data analysis"

Abstract booklet

October 9th, 2020, 09:00 – 16:30

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9th European Nanoanalysis Symposium

"Nano-scale materials characterization - Advances in data acquisition and data analysis"

Research and development in materials characterization techniques are increasingly needed for modern materials science, for innovation in high-tech branches and to guarantee the functionality, performance and reliability of advanced products. The sustained progress materials science and engineering is increasingly driven by computational materials science, multi-scale modeling and characterization. More than ever before, materials-driven product innovations in industry and shorter time-to-market introductions for new products require high advancement rates and a tight coupling between research, development and manufacturing. Analytical techniques and respective tools, particularly to investigate nanomaterials, are considered to be fundamental drivers for innovation in industry.

As a consequence, this symposium will cover the topics of nanoanalysis and materials characterization along the whole value and innovation chain, from fundamental research up to industrial applications. It will bring scientists and engineers together from universities, research institutions, equipment manufacturers and industrial end-users. New results in disruptive nanoanalysis techniques will be reported in several talks and in the poster sessions, and novel solutions in the field of materials characterization for process and quality control will be shown. The discussions and interactions between the stakeholders will help to identify gaps in the fields of advancing nanoanalysis and materials characterization and to propose actions to close them and to support industrial exploitation of innovative materials. The symposium aims at reinforcing ongoing collaborations and discussing ideas for new collaborations.

Proceedings



All participants are invited to publish their work as a full paper in the open-access-journal Nanomaterials by MDPI.

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(submission deadline: December 10, 2020)

Symposium Chairpersons

- Ehrenfried Zschech, (main organizer), Fraunhofer IKTS Dresden, Germany
- Eva Olsson, Chalmers University of Technology, Gothenburg, Sweden
- Rodrigo Martins, FCT–UNL, Lisbon, Portugal
- Sabrina Sartori, University of Oslo, Norway
- Robert Sinclair, Stanford University, Palo Alto/CA, USA

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- Gerd Schneider, Helmholtz-Zentrum, Berlin, Germany
- Olivier Thomas, University Marseille, France
- Oden Warren, Bruker, Minnesota, USA
- Thomas Weissgaerber, Fraunhofer IFAM, Dresden, Germany

Invited speakers

- Alexander Soldatov, Southern Federal University, Rostov-on-Don, Russia
- Gerd Schneider, Helmholtz-Zentrum Berlin, Germany
- Krzysztof Wozniak, University Warsaw, Poland
- Marco Sebastiani, Universita Roma Tre, Rome, Italy
- Mathias Mosig, Protochips, Berlin, Germany
- Jan Neuman, Nenovision, Brno, Czech Republic
- Jiri Dluhos, Tescan Orsay Holding, Brno, Czech Republic
- Lukas Palatinus, Czech Academy of Science, Institute of Physics, Prague, Czech Republic

Program

Welcome and introduction (9:00-9:10)

Ehrenfried Zschech, Fraunhofer IKTS Dresden, Germany

SESSION 1: X-ray techniques – Session Chair: Ehrenfried Zschech

9:10 - 9:35

1.1 *"Big Data and AI algorithms for the analysis of X-ray spectroscopy data"* Alexander Soldatov, Southern Federal University, Rostov-on-Don, Russia

9:35 - 10:00

1.2 "Nanoscale X-ray spectromicroscopy at BESSY" Gerd Schneider, Helmholtz-Zentrum Berlin, Germany

10:00 - 10:25

1.3 *"A century after the Braggs and Max von Laue: Quantum Crystallography"* Krzysztof Wozniak, University Warsaw, Poland

Break (10:25-10:35)

SESSION 2: Nanomechanics – Session Chair: Rodrigo Martins

10:35 - 11:00

2.1 *"Nanoscale residual stress mapping in multilayer thin films"* Marco Sebastiani, Universita Roma Tre, Rome, Italy

POSTER SESSION P1 (11:00-11:45) – Session Chair: Paweł Zięba

Break (11:45-11:55)

SESSION 3: Attachments to microscopes – Session Chair: Gerd Schneider

11:55 – 12:20

3.1 "AXON - Delivering on the Promise of Atomic Scale Dynamics" Mathias Mosig, Protochips, Berlin, Germany

12:20 - 12:45

3.2 *"AFM-in-SEM: The novel approach to correlative microscopy and advanced surface characterization"* Jan Neuman, Nenovision, Brno, Czech Republic

POSTER SESSION P2 (12:45-13:10) – Session Chair: Małgorzata Lewandowska

Lunch break (13:15-14:15)

SESSION 4: Electron microscopy – Session Chair: Eva Olsson

14:15 - 14:40

4.1 *"Multi-modal materials characterization with the latest plasma FIB-SEM"* Jiri Dluhos, Tescan Orsay Holding, Brno, Czech Republic

14:40 - 15:05

4.2 "Electron nanocrystallography – a new tool for materials science" Lukas Palatinus, Czech Academy of Science, Institute of Physics, Prague, Czech Republic

POSTER SESSION P3 (15:05-16:20) – Session Chair: Sabrina Sartori

Wrap-up, closing remarks (16:20-16:30)

Ehrenfried Zschech, Fraunhofer IKTS Dresden, Germany

Poster Presentations

POSTER SESSION P1

P1.1	Twinning and shear banding in copper and Cu-14%wt. Al alloy single crystals of {112}< 111> orientation deformed in channel-die	Izabela Mania
P1.2	Cu / Ag nanodroplet wetting graphene / coated Cu substrate: combine studies	Aleksandra Drewienkiewicz
P1.3	Effect of stress on microstructure and mechanical properties of high carbon steel during bainitic transformation	Karol Janus
P1.4	Study of the strength of (Cr3C2-25(Ni20Cr))-5(Ni25C) composite coatings deposited on the Al 7075 substrate	Anna Trelka
P1.5	The influence of high-temperature annealing on the microstructure and hardness of L-DED Inconel 625	Kewin Gola
P1.6	Metallurgical characterization of Cu-based memorial medals	lwona Gasiorowska
P1.7	Applications of a novel in-situ four-point bending device for materials analysis	Christoph Sander
P1.8	A preliminary study on fabrication of diatomaceous earth/aluminium MMCs by spark plasma sintering technique	Magdalena Lepicka
P1.9	The influence of capillary pores on transport of chloride ions / numerical simulations in nano-XCT based 3D cementitious microst	Jakub Stec
P1.10	Microstructure and mechanical behavior of fossil diatom frustules Ellerbeckia baileyi and Melosira undulata	Qiong Li
P1.11	A combined soft and hard XPS study of the oxidation behaviour of post- deposition annealed titanium-tungsten diffusion barriers	Curran Kalha
P1.12	Small Amphiphilic Ligand-based Synthesis of Hydroxyapatite Nanoparticle for Titanium Implant Coating: Characterization& Analysis	Priya Mullick
P1.13	Gold-coated silicon nanowire arrays for molecular sensing using surface- enhanced Raman spectroscopy	Ekaterina Alekseeva
P1.14	Nano-mechanical and nano-tribological investigation of metallic and carbonitride TiCrCoNiV high entropy alloys	Mihaela Dinu
P1.15	Preparation and investigation of plasmonic properties of Ag/Au alloys	Ana-Maria Iordache
	POSTER SESSION P2	
P2.1	Microstructure and catalytic activity of Al13Co4 melt spun alloy	Amelia Zięba
P2.2	Microstructure and phase composition of refractory ceramic shielding thermally exposed parts in steel making process	Marcin Prochwicz
P2.3	Influence of W addition on microstructure and properties of TiB2-W coatings	Edyta Chudzik

P2.4	Generating new excitation pathways for green emission of InGaN/GaN MQWs by Xe swift heavy ion irradiation	Jose Pedro de Cardoso
P2.5	Microstructure investigation of silicon nitride-zirconia-graphene composite using multi-scale microscopy	Zhongquan Liao
P2.6	ZnO low-dimensional nanostructured porous thin films for photocatalytic degradation of methylene blue in water purification	Anna Kuliś- Kapuścińska
P2.7	Preparation of nanoceramic materials and composites by needleless electrospinning	Ivan Shepa
P2.8	Diatoms' frustules as a possible natural filler in composite materials	Izabela Zgłobicka
P2.9	A novel approach to evaluate mechanical BEoL stack stability utilizing Cupillar shear off and acoustic emission	Jendrik Silomon
P2.10	Structural and Electronic Effects of X-ray Radiation on Prototypical Catalysts	Nathalie Fernando
	POSTER SESSION P3	
P3.1	Thermodynamic properties of selected liquid lithium alloys	Miłosz Zabrocki
P3.2	Influence of different types of catalysts on pyrolysis process	Małgorzata Sieradzka
P3.3	Sustainable materials applied to flexible electronics using a laser induced modular platform	Sara Silvestre
P3.4	Effect of mechanical deformation on organic electronics based on novel two-dimensional polymers	Bowen Zhang
P3.5	Synthesis of nano-sized metal organic framework using selectively modified clay nanotube for enhanced gas adsorption properties	Sooji Park
P3.6	Slow disassembly of the germanosilicate UTL	Ondřej Veselý
P3.7	Utilization of unique organic materials deposited by Atomic Layer Injection method	Tomas Krajnak
P3.8	Synthesis of metal@molecular sieve composite catalysts with bimetallic nanoparticles for hydrogenation reactions	Anastasia Kurbanova
P3.9	Mechanical Reinforcement of Polymer Colloidal Crystals by Supercritical Fluids	Visnja Babacic
P3.10	Mechanical and tribological characterization of (TiAl0.5CrNbY)Nx high entropy alloys: from micro- to nano-scale	Iulian Pana
P3.11	Structural and photoluminescent properties of porous silicon nanowires fabricated by MACE: influence of H2O2 concentration	Daniil Moiseev
P3.13	Atomic resolution microscopy reveals the growth mechanism of 2D-CuO agglomerates synthesized via pulsed spark discharges	Marta Agati

P3.14	Pure Blue Fluorescent Organic Light Emitting Diode with an External Quantum Efficiency Near to the Theoretical Limit	Dhruvajyoti Barah
P3.15	High efficiency third generation oled using near infra red (NIR) material TPA-DCPP	Naga Sai Manoj Inaganti
P3.16	Electrophysical anisotropy of amorphous silicon surfaces nanocrystallized by femtosecond laser pulses	Dmitrii Shuleiko
P3.17	Tuning the magnetic anisotropy of SrFe12O19 nanocrystallites	Pierfrancesco Maltoni
P3.18	Multiscale Simulation Framework for Functional Polymers	Steffen Kampmann
P3.19	Biodegradable porous silicon nanoparticles produced from silicon nanowires	Daria Maksutova
P3.20	Diagnostic and radiotherapy improvement employing metallic biocompatible nanoparticles	Alfio Torrisi
P3.21	Nanodiamond Magnetometry for localized free radicals detection in sperm cells	Aldona Mzyk
P3.24	Probing deep trap states in P3HT using electroabsorption spectroscopy	Subhamoy Sahoo
P3.25	A hybrid of reduced graphene oxide grafted amine-functionalized NiO/ZnO toward attenuation of electromagnetic waves	Quyen Vu Thi
P3.26	Electrochemical assessment of two metallo-porphyrins (Mn&Zn) for histamine detection - application in fresh meat evaluation	Ana-Maria Iordache

Abstracts

-Talks-

Big Data and AI algorithms for the analysis of X-ray spectroscopy data

A. Soldatov*1, A. Guda1, A. Martini1,2, S. Guda1, A. Bugaev 1

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Modern synchrotron radiation sources and even laboratory devices produces now really Big spectroscopic Data while studying transformations of the materials during the processes, such as charge-discharge of metal-ion batteries, catalytical reactions or fast photoinduced transformations.

XANES region of X-ray absorption spectrum should be sensitive to the coordinates of all atoms in the local cluster around x-ray absorbing atom. In contrast to X-ray diffraction, a quantitative analysis of XANES spectra is rarely performed till now, especially in the case of Big Data sets obtained. The main reason is the larger amount of time required for theoretical analysis of a single XANES spectrum compared to X-ray diffractogram. For such time-consuming calculations, in the space of several structural parameters, we developed an interpolation approach based on machine learning algorithms [1]. Machine learning is an emerging tool for quantitative analysis of XANES spectra. The spectrum contains all information about local atomic structure around absorbing atom. The ultimate goal would be predicting xyz coordinates from a given spectrum in a similar way it is done in single crystal diffraction. Due to approximations in the theoretical description, limited energy range, experimental artefacts and correlations such approach is not established yet. Current applications of XANES to quantitative structural refinement using both local descent approaches and neural networks provide no estimations to the number of possible structural parameters that can be refined. It is not clear a priori how much structural parameters and with what precision can be refined. Our work determines the type of structural information, which can be extracted from a spectrum on the basis of descriptor concept. We provide a methodology to analyze the theoretical training set first before its application for refinement. As an additional result we show geometrical interpretation of the several descriptors of XANES.

We have chosen Jupyter Notebook framework to be friendly for users and at the same time being available for remastering [2]. The analytical work is divided in two steps. First, the series of experimental spectra are analyzed statistically and decomposed into principal components. Second, pure spectral profiles, recovered by principal components, are fitted by theoretical interpolated spectra. We implemented different schemes of choice of nodes for approximation and learning algorithms including Gradient Boosting of Random Trees, Radial Basis Functions and Neural Networks. The fitting procedure can be performed both for a XANES spectrum or for a difference spectrum, thus minimizing the systematic errors of theoretical simulations. The problem of several local minima is addressed in the framework of direct and indirect approaches.

Acknowledgments.

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References

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Nanoscale X-ray spectromicroscopy at BESSY II

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In the nano-age, humans manufacture complex structures atom by atom to design e.g. their specific functionality. Therefore, new tools for the analysis of these structures have to be developed. The HZB microscopy group develops novel methods for X-ray imaging to make use out of the unique interactions of X-rays with matter. For this, X-ray optics for the 10-nm scale characterization of the nanostructure, chemical nature, and composition of materials with high energy resolution are engineered and fabricated. The HZB full-field TXM at the BESSY II U41 undulator beamline allows high spectral resolution of $E/\Delta E$ =5000, about 10 nm (half-pitch) spatial resolution and field of views in the range of 10-15 µm [1-4]. With this instrument spatially-resolved NEXAFS studies for material sciences can be performed due to the high energy resolution [5]. Additionally, nano-tomography of cryogenic samples had demonstrated its high potential for life sciences [2].



Fig. 1: X-ray optical setup the the full-field transmission X-ray microscope installed at BESSY II in Berlin. Nanoscale NEXAFS spectroscopy is performed by collecting an image stack in small photon energy steps at X-ray absorption edges.

Conventional spectroscopy methods such as photoemission spectroscopy and X-ray absorption spectroscopy have shown to be particularly well-adapted probes to study electronic properties of nanostructures. However, these conventional spectroscopy techniques typically illuminate areas of 50 μ m x 50 μ m or larger thus preventing the analysis of a single nanostructure. Spectromicroscopy investigations with nanometer resolution were restricted so far to scanning X-ray microscopes (STXM) or to transmission electron microscopes (TEM) equipped with electron energy loss spectroscopy (EELS).

Both methods give no statistical information as they are restricted to small image fields. In contrast, the typical image field in NEXAFS spectroscopy measurements combined with full-field transmission X-ray microscopy (NEXAFS-TXM) is about 10 μ m x 10 μ m which is large compared to the individual nanoparticle. Therefore, one image stack already contains statistically significant data with nanometer resolution.

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A century after the Braggs and Max von Laue: Quantum Crystallography

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This is quite a paradox that a century after the introduction of the Independent Atom Model (IAM -Bragg, 1914), 99.7% of all ca. 1.5mln known crystal structures have been refined using IAM which has some methodological deficiencies. This, among others, includes structures of almost all minerals. In IAM atoms are defined as spheres which do not exchange electron density. In my presentation, I will present a few modern quantum crystallographic aspherical approaches to refinement of structures and localization and refinement of H-atoms[1] such as the Hansen-Coppens pseudoatom formalism applied in multipole modeling [2] and Hirshfeld Atom Refinement (HAR) [3]. I will present a detailed comparison of the results obtained with different approaches as a function of data resolution and models of electron density and compare these with the results of neutron diffraction and theoretical computations. I will also discuss the accuracy and precision of different refinement results. I will also present a few selected examples of quantum crystallographic studies showing, among others, redistribution of charge in minerals under pressure.

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Nanoscale residual stress mapping in multilayer thin films

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Silver-based low-emissivity (low-E) coatings are used on transparent building elements (windows) to optimize heat losses. They generally consist of dielectric/Ag/dielectric multilayer stacks, where the thin Ag layer reflects long wavelength infrared (IR), while the dielectric layers both protect the Ag and act as an anti-reflective barrier. The sequence of layers in these films can influence the mechanical properties, which are also strongly related to the nano-scale residual stress distribution in the stack. Residual stress evaluation by combining focused ion beam (FIB) milling and digital image correlation (DIC), using the micro-ring core configuration (FIB-DIC), offers micron-scale lateral resolution and provides information on the depth variation of residual stress, even for non- equibiaxial stress distributions, and hence can be effectively used to characterize low-E coatings.

In this work, we propose an innovative approach to improve the depth resolution and surface sensitivity for residual stress depth profiling in the case of ultra-thin as-deposited and post-deposition annealed Si3N4/Ag/ZnO low-E coatings, by considering different fractions of area for DIC strain analysis and accordingly developing a unique influence function to maintain the sensitivity of the technique at is maximum during the calculation. Residual stress measurements performed using this novel FIB-DIC approach revealed that the individual Si3N4/ZnO layers in the multilayer stack are under different amounts of compressive stresses. The magnitude and orientation of the stress change significantly after heat treatment and provides an explanation for the observed differences in terms of scratch critical load. The results show that the proposed FIB-DIC combined-areas approach is a unique method for probing non-equibiaxial residual stresses with nano-scale resolution in thin films, including multilayers.



Figure 1. Schematic representation of the novel FIB-DIC procedure here presented..

Acknowledgments

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number 760827, https://cordis.europa.eu/project/id/760827, www.oyster-project.eu

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AXON - Delivering on the Promise of Atomic Scale Dynamics

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Resolving the redox reaction of metallic nanoparticles is crucial to improve their application in many different fields. The in situ or operando TEM technology is attractive in observing sample dynamics that provides unique insights into the reaction mechanisms.

However, the data acquisition is challenging due to inherent imaging instability caused by external stimuli of both chemical and physical fields (e.g. temperature). The redox reaction has not been precisely captured due to compromised data quality or missing moments of sample dynamics.

The advanced TEM platform AXON enables intelligent control of such experiment, ensuring that sample stays locked in place as environmental conditions change, delivering unprecedented results even at extreme magnifications. Along with fully synchronized data collection, the redox of copper (oxide) NPs is well-resolved in space and time triggered by a variety of thermal and chemical environments. The nanoscale Kirkendall effect, formation of oxidation islands and reduction densification was visualized in real time. AXON enhanced analysis and resolution capability of TEM and empowers new types of research to unlock applications in relevant fields.

References

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3.1

AFM-in-SEM: The novel approach to correlative microscopy and advanced surface characterization

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Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are two of the most used, complementary techniques for surface analysis at the nanoscale. Thus, combining them by integrating a compact AFM into SEM brings novel possibilities for true correlative imaging and advanced multi-modal sample characterization that would be often unfeasible using each imaging modality separately. LiteScope is produced by the NenoVision company and represents a compact AFM, which is designed to be integrated into a large variety of SEMs in a plug-and-play manner. In general, the strength of the AFM-in-SEM hybrid system lies in combining the AFM modes (3D topography, electrical, mechanical and magnetic measurements) with SEM capabilities (fast imaging with wide resolution range, chemical analysis, surface modification using FIB/GIS etc.). Further benefits include precise AFM tip navigation by SEM to the region of interest, roughness evaluation and in-situ conditions, which is essential for sensitive samples and minimizes sample handling. Uniquely, LiteScope design enables simultaneous acquisition and correlation of AFM and SEM data by NenoVision?s proprietary technique called Correlative Probe and Electron Microscopy (CPEM).

CPEM functionates in a way that the electron beam and AFM tip keep a constant offset and remain static during the image acquisition. The scanning movement is conducted by a piezo scanner that carries the sample. This ensures simultaneous SEM and AFM data collection in the same coordinate system and with identical pixel size. The resulting 3D CPEM view can combine multiple channels, both from AFM and SEM, enabling thorough sample analysis and clear data interpretation for specific applications.

In conclusion, the AFM-in-SEM strategy benefits from the complementarity of both techniques alongside significant savings both in time and resources. Also, it opens completely new possibilities for advanced data correlation and measurements in variety of industrial and research applications, such as semiconductors, material-, biological- and earth-sciences.

3.2

4.1

INVITED TALK

Multi-modal materials characterization with the latest plasma FIB-SEM

Jiri Dluhos

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TBA

Electron nanocrystallography – a new tool for materials science

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Modern material science, chemistry and biochemistry work with more and more complex materials and synthetic routes that often do not yield large single crystals. If the maximum available crystal size reaches only a few hundred nanometres or even less, the only practically feasible approach to single crystal structure analysis is the application of electron diffraction.

Single crystal structure analysis by electron diffraction faces a number of fundamental as well as technical problems. However, many of these problems have been at least partly solved in the past few years, and the fast development of the method has received a lot of attention and positive reception in the crystallographic and materials-science community.

At present, three-dimensional electron diffraction (3D ED) methods are being used in many laboratories almost routinely to analyze the crystal structures of a wide variety of materials, ranging from metals, oxides and other inorganic materials through minerals, framework and porous materials to organic molecular crystals and macromolecular crystals [1].

The lecture will briefly review the basics and history of the 3D ED methods and illustrate its potential on three selected examples – semiconducting tantalum trisulphide, structure determination of a new phase in the Ni-Ti system and analysis of carbon-dioxide adsorption in nanocrystalline zeolite.

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4.2

Abstracts

- Poster presentations -

P1.1 winning and shear banding in copper and Cu-14%wt. Al alloy single crystals of {112}< 111> orientation deformed in channel-die

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High strain rate deformation processes such as ballistic impact, metal cutting or blast loading results in the formation of intense localized regions in the form of narrow bands, called adiabatic shear bands (ASB). They were firstly described by Zener and Hollomon in 1944 [1] as a unique mechanism of a material or structural instability often leading to a catastrophic failure [2] induced by intense localized raise of temperature during the process [3, 4]. However, the details of the mechanism of ASB nucleation, thickening and propagation as well as the crystallographic determinations of these processes are still not well-recognized. In this work, the influence of twinning and micro- and macro- scale shear banding on microstructural and textural changes was investigated in high purity Cu and Cu-14%wt. Al alloy in order to characterize the mechanism of ASB formation. These changes were characterized over a wide range of scales including optical microscopy, scanning electron microscopy equipped with highresolution electron backscatter diffraction facility (SEM/EBSD) and transmission electron microscopy (TEM). For simplicity the analyses were focused on description of the mechanism of the ASB formation in single crystalline samples of C{112}< 111> initial orientation, deformed in channel-die up to 60% at strain rate of ~ 5000 s-1. The detonation of the explosive charge was used for propel of the punch in a channel-die. During plane strain deformation at 'conventional' strain rates, two kinds of shear bands are observed depending on the stacking fault energy (SFE). If the precursory obstacles for dislocation motion are fine twin-matrix lamellae, typical for metals with low SFE (e.g. in Cu-14%wt.Al alloy) the SBs are classified as 'brass-type'. If the precursory obstacles are the elongated dislocation walls of a cell block structure the shear bands are of the 'copper-type'. They are typically observed in materials with high or medium SFE (e.g. in Cu deformed at ?conventional? strain rates). At extremely high strain rates the deformation behavior of both metals is qualitatively similar, since the only brasstype shear bands are observed in Cu and Cu-14%wt.Al alloy. In the both cases the precursory obstacles for dislocations motion are formed by three families of the deformation twins clusters. (It is important to note that the deformed matrix is almost completely consumed by twins). The rotation-induced mechanical instability within narrow areas of the anisotropic structure of twin-matrix layers leads ?via? kink-type bands to the formation of welldeveloped shear bands. This is crucial for understanding further texture transformations and for explanation of the crystallographic nature of the ASB. It was shown how the pre-existing sub-structures of twin-matrix layers are incorporated into ASB area, and what kind of the dislocation mechanism is responsible for strain accommodation at macro-scale. From crystallographic point of view it was found that the re-orientation of the {111} twinningplane (also the plane of co-planar slip systems) towards the ASB plane facilitates further dislocation slip in the shear direction. Finally, referring to the idea of local lattice re-orientation [5, 6] a crystallographic model of the ASB formation in fcc metals is proposed.

Acknowledgments

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P1.2 Cu - Ag nanodroplet wetting graphene / coated Cu substrate: combine studies

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Graphene is a two-dimensional material, which has a great potential for many future applications considering its extraordinary electrical, mechanical, and optical properties [1]. It can be used as a membrane material due to its honeycomb structure, for which the distance between carbon atoms is on the order of 0,064 nm. Thus, the layer of graphene is a barrier material for most gases, excepting hydrogen ions (protons), which has smaller radius [2]. Graphene can also serve as an oxidation protective layer for materials like Cu or Ni [3, 4]. It may influence wetting by liquids as well as dynamics of processes occurring at the interface while deposited onto solid substrate [2]. Interactions between atoms and their spatial distribution near the solid-liquid interface are important factors for the determination of wettability of material as well as crucial in phenomena occurring at the interface in chemical, biological, and technological systems. Especially, graphene seems to be a promising material in electronics industry to limit the diffusion between a substrate and wetting substance, and so, to reduce the growth of compounds such as Intermetallic Compounds (IMCs) which can form at interface [5]. Excessive growth of IMCs is highly undesirable due to the enhanced brittleness, hardness and reduced ductility of the joints. As a consequence depositing layer of graphene could enhance properties of formed joints and their reliability. Wetting is one of the main factor in the case of creating metal contacts. The wetting behavior induced by graphene layer deposition has been investigated mainly using droplets of water and pure metals as wetting substances. So far, some disagreements are found for a correct description of an interaction of graphene with water-based on the experimental results published. Nguyen et al. [6] performed molecular simulations to depict the differences in contact angle between water droplet and substrates such as pure bare Cu and graphene ? coated Cu. They also discussed the wetting transparency phenomena in a view of the results found in literature [7]. Only few papers presenting atomistic simulations have been delivered for metal droplets, including interactions with Hg [8], Al and Pb [9], Cu [10], Fe [11], Pd and Ti [12], as well as Ag [13]. However, pure metals are rarely used in technical solutions due to their poor mechanical properties, and thereby, alloys are more convenient solution. As yet, no insight into the interactions between a Cu-based alloy nanodroplets and graphene/metal interface has been published. Moreover, the impact of wetting on the structureproperties interplay has not been investigated. Herein, we discuss structure, composition and interfacial properties of a Cu-Ag nanodroplet in contact with a graphene-coated Cu matrix by atomistic simulations compared with our new experimental results. Structural and dynamic properties of the nanodroplet near the graphene-coated substrate have been studied as a function of graphene structure. The performed atomistic simulations allowed us to understand the structural transitions in the drop by analyzing chemical and topological atom order in Cu ?Ag alloy and kinetics at the solid-liquid interface. In this work, we investigated four systems. Copper foil was used as a substrate in all cases: for the two of them, graphene was deposited using chemical vapour deposition method (CVD), in order to obtain diffusion barrier, while two left samples were kept free of graphene layer on the Cu outermost surface. We have used two wetting substances for those variants, such as pure Ag and eutectic Ag-Cu alloy. All of the investigated samples were heated up to T = 1323 K. Our preliminary experimental results clearly show that graphene layer has an impact on diffusion occurring between substrate and the droplets. In case of samples with no graphene deposited on Cu surface, the change in their shape was observed. Namely, a melted alloy of sphere shape was formed from the substrate and wetting substance. Moreover, there was no interface area, which indicates that the reaction between foil and droplets occurred in the entire volume of the investigated material, leading to an alloy formation. Contrary, the interface region could be easily identified for graphene/Cu matrix interface. After heating, samples with a drop adhered to the Cu substrate were observed. Scanning Electron Microscope (SEM) with Energy-dispersive X-Ray Spectrometer (EDS) was used to investigate the microstructure and chemical composition of samples. Images taken with SEM confirm our observations in macro scale. For variants with graphene layer, the interface between droplet and the substrate is well defined. The presence of graphene on the Cu matrix limits the diffusion between substrates and droplets, but it does not hinder Cu substrate before wetting. EDS spectroscopy was also used to determine the changes in chemical composition. For the variants with no graphene layer deposited on a Cu substrate, all of the samples have an uniform and two-phase structure as compared to interfaces with graphene for which only the droplets have two-phase structure. Structure of the samples with graphene layer, was also investigated using Raman Spectroscopy. For all the system configurations, atomistic simulations using molecular dynamics have been performed. We have compared them to the results obtained from the experiment.

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graphene, interface, wetting, molecular dynamics, structure, diffusion, nano

P1.3 Effect of stress on microstructure and mechanical properties of high carbon steel during bainitic transformation

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High-carbon carbide-free bainitic steels represent a new generation of materials, with optimal strength to plasticity ratio. The excellent properties of the steels are obtained mainly due to the formation of a nanostructure consisting of extremely fine plates of bainitic ferrite, 20-40 nm thick, embedded in the matrix of austenite without carbides at ferrite/austenite boundaries. The nanostructured bainitic steels are generated through isothermal bainitic transformation at low temperatures but above the martensite start one kept for long times (e.g. isothermal heat treatment can take from 2 to 60 days over the range of 125-325°, respectively), adding a significant cost to the product. However, in a commercial scenario, there may be need for more rapid heat treatment in order to limit the cost of production [1-4]. The transformation can be accelerated by (i) the addition of alloying elements like Co and Al, (ii) increasing prior austenite grain size and therefore austenitization temperature [5, 6]. The application of stress at bainitic temperature transformation is another way to reach the same effect. The new modification of the technology will shorten the time of isothermal treatment, reduce the size of nanobainite colonies and the degree of texture of deformed elements. It is possible through the generation of complex deformation (the direction and intensity of which will be controlled) leading to austenite shear at the transformation temperature, during which the bainite strips are induced alternately in the entire volume [7-11]. The aim of the presented work is to study the influence of various combinations of stress (compressive, tensile and torsion) during isothermal bainitic transformation on microstructure and mechanical properties of the steel. The hot-rolled and spheroidized steel with following composition: Fe-0.74C-2.64Si-1.82Mn-1.00Ni- 0.36Mo-0.21Cr-0.047Al (wt. %) was machined into cylindrical samples of reduced section 10 mm in diameter of and the length of 18 mm. The thermomechanical treatment was conducted using a Bähr MDS 830 simulator dedicated for physical simulation of materials processing described below. After the thermomechanical treatment all samples were held for 10 min at the temperature of deformation and next cooled to RT, but first the specimens were heated to austenitization temperature of 950°C at 2,5 K/s and kept for 3 min. Then, the bainitic transformation procedure was induced by holding the steels at: (i) 230 °C single torsioned by 180° (true strain ~0,32, strain rate 0,03 1/s), (ii) 200 °C, torsion 100° at axial tension (true strain 0,07), stress strain rate 0,07 1/s, (iii) 200 °C torsion 100° (0,07 1/s) at axial compressive stress, strain rate 0,07 1/s. The metallographic study of the all samples after thermomechanical treatment showed that they consisted of bainitic structure. It proved that applying single torsion or combination of torsion with compression/tension at temperature above MS leads to acceleration of bainitic transformation by several times. The detailed identification of structure morphology was not easy using optical microscopy only, therefore the studies of microstructures using higher magnification were performed. The TEM micrographs of the sample after isothermal treatment at 200°C at torsion 100° and axially tensioned, which confirmed the presence of two separate phases: carbide-free bainite, which consisted of mixture of carbon supersaturated ferrite plates with the average thickness of 200-300 nm, and the retained austenite with the thickness of 50-300 nm. The XRD studies confirmed that the concentration of austenite decreased from 29.2 to 24.5 vol.% for the samples after single torsion and after those torsioned and compressed, respectively. The tensile strength test results of the steel samples after austenitization at 950°C/3 min and cooling followed by isothermal treatment with torsion, torsion with

tension, torsion with compression, and strength after hot rolling and typical heat treatment 950°C for 30 min, completed with annealing for 72 h at 200°C shows that the highest properties were registered for the sample after single torsion due to the arrangement of bainite plates in one direction. The application of complex stresses led to the decrease of mechanical properties connected with the random direction of plate growth and their mutual blocking during coarsening. When comparing new thermomechanical treatment with the conventional nanobainitic one it could be seen that their mechanical properties were about 30% lower, nevertheless, the heat treatment time was significantly reduced. Further studies are required to optimize the thermo-mechanical treatment of the examined steels.

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P1.4 Study of the strength of (Cr3C2-25(Ni20Cr))-5(Ni25C) composite coatings deposited on the Al 7075 substrate

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In recent years, the cermet composite coatings produced by cold spraying are often used in various industries such as automotive and aerospace mainly for application to machine part. The main advantage of using this type of coating is very good mechanical properties, obtained by strengthening the metallic matrix with ceramic phase particles. A key aspect is also the high adhesion of the coatings to the substrate, allowing them to work intensively without the effect of peeling off from the substrate [1-3]. The paper presents the analysis of microstructure and strength (Cr3C2-25(Ni20Cr))-5(Ni25C) composite coatings in the interface with the AI 7075 substrate before and after adhesion and threepoint bending test. The cold spraying process was performed with an Impact Innovations 5/8 system mounted on a Fanuc M-20iA robotic arm. The tests of coatings using X-ray diffraction using a Bruker D8 Discover diffractometer methods allowed the identification of the phase composition of the sprayed coatings. Characterisation of the microstructure was made based on observations carried out using the scanning electron microscope FEI E-SEM XL 30. To investigate the coating microstructure in micro/nanoscale areas FEI TECNAI G2 transmission electron microscope (TEM) was using. The thin foils for transmission electron microscopy studies were cut with a FIB technique using an FEI QUANTA 3D Dual Beam. The coating hardness test (HV0.3) according to the standard [4] referred to as the Vickers hardness test at low loading force was carried out on a device of the company CSM Instruments SA. The adhesion test was carried out by Positest AT-A device. The three-point bending test was performed with the INSTRON 6025 device. X-ray diffraction studies showed only phases occurring in the initial powder which proves that there were no changes in the phase composition of the coating during the cold spraying process. The microstructure observations revealed a homogeneous distribution of phases in the coating and embedded ceramic particles in the substrate. The hardness of cold sprayed coatings was in the range of 600 ? 650 HV0.3. A slight differentiation of the coating hardness was observed, especially between that measured in its middle zone and that near the coating-substrate interface. The study of the adhesion of (Cr3C2-25(Ni20Cr))-5(Ni25C) coatings on the AI 7075 substrate showed that the different preparation (e.g. sandblasting) of the substrate does not affect the final measurement results. Three-point bending tests were carried to investigate the mechanical and bonding properties of the coating to the substrate. (Cr3C2-25(Ni20Cr))-5(Ni25C) coating is a rigid and brittle material and has very limited deformation capability. In the 3-point bending test, the coating matches the bend deformation of the substrate by transversal and interfacial cracking. The denser and finer transversal cracks indicate the coating having a good spalling resistance. Similar relationships were found during mechanical tests of thermally sprayed WC-Co-Cr coatings in [5]. The resent study presents the attempt to test of the adhesion and mechanical properties of (Cr3C2-25(Ni20Cr))- 5(Ni25C) composite coatings in contact with the substrate Al 7075 correlate them with microstructure observation. The coatings showed high hardness, good adhesion to the substrate and a compact microstructure without discontinuities and porosity.

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P1.5 The influence of high-temperature annealing on the microstructure and hardness of L-DED Inconel 625

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Inconel 625 is a nickel-based superalloy characterized by high strength and corrosion resistance at high temperature up to 800 °C. These features made it to be commonly used in the chemical industry, aerospace and power plant applications. On the other hand, Inconel 625 exhibits high hardness, poor machinability and low thermal conductivity, thus it is difficult to fabricate components with a complicated shape. These problems can be overcome through the use of additive manufacturing. Laserbased directed energy deposition (L-DED), one of the major additive manufacturing processes, consists of melting metal powder fed by nozzle by a focused laser beam. This process is mainly used to repair and recover metal parts, however, it can be also used for fabrication of the whole parts. Application of L-DED Inconel 625 at a high temperature requires investigation of its influence on microstructure and hardness. Therefore, the aim of this study is a microstructural investigation and microhardness measurements of Inconel 625 additively manufactured using the L-DED method, subjected to stress relief annealing at a temperature of 870 °C for 1 hour and subsequently annealed at a temperature of 600, 700 and 800 °C for 5 hours. Microstructural investigation was carried out by light microscopy, scanning electron microscopy combined with microanalysis of chemical composition by energydispersive X-ray spectroscopy. Phase identification was performed with the use of electron diffraction in the transmission electron microscope. For microhardness measurements, the Vickers HV1 method was used.

It was found that after stress relief annealing L-DED Inconel 625 exhibits fine dendritic microstructure, which is typical for metal alloys processed by this method. Precipitates of the secondary phases, which are irregular, globular and plate-like shaped, segregate to the interdendritic regions (fig. 1a). They have been identified as Laves phase, MC and M23C6 carbides. After annealing at a temperature of 600 °C, there were no visible differences in microstructure comparing to stress-relieved condition (fig. 1b). In turn, after annealing at a temperature of 700 °C a lower amount of the irregular-shaped precipitates of the Laves phase was noticed, with a simultaneous increase of the population of plate-like precipitates of the delta phase enriched in Nb and Mo. Moreover, the dendritic microstructure disappeared due to the homogenization of the chemical composition (fig. 1c). Further increasing of the annealing temperature up to 800 °C led to the disappearance of the Laves phase in favour of the further precipitation and growth of the delta phase precipitates (fig. 1d).



Figure 1. Microstructure of Inconel 625 fabricated by L-DED stress-relieved at a temperature of 870 °C for 1 hour (a) and subsequently annealed for 5 hours at a temperature of b) 600 °C, c) 700 °C and d) 800 °C

The evolution of the microstructure was correlated with the changes in the hardness. The average hardness of the stress relieved Inconel 625 was 274 HV1 and after annealing at a temperature of 600, 700 and 800 °C was respectively equal to 289, 303 and 279 HV1 (fig. 2). The increase in hardness achieved after annealing at a temperature of 600 and 700 °C is caused by a precipitation hardening due to the precipitation of particles from the supersaturated solid solution. The maximum hardness is achieved at a temperature of 700 °C and subsequently diminishes after annealing at a higher temperature of 800 °C due to the overaging.



Figure 2. The average hardness of Inconel 625 fabricated by L-DED stress-relieved at a temperature of 870 °C for 1 hour and subsequently annealed at a temperature of 600, 700 and 800 °C for 5 hours.

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Metallurgical characterization of Cu-based memorial medals

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Two gilded Kaiser Wilhelm memorial medals with similar appearance were studied using nondestructive and destructive techniques to determine the chemical composition of the base materials. The two medals consist of low-alloyed Cu (medal B) and CuZn7Sn3 (medal A), with some additional trace elements. We conclude that apart similar appearance medals A and B were manufactured differently, most probably in different mints.

Introduction

The concept of Preventive Conservation (PC) of cultural artefacts in museums and collections is based on mitigation of the deterioration or damage due to material ageing as well as biological, mechanical and chemical degradation processes on-going over time. The degradation of an artefact – depending on the environmental conditions to which it is exposed – has to be described and modelled. The PC models have to be specific for each class of materials, and they have to be validated by experimental data [1]. For metal objects, changes of the surface and of the sub-surface domain, e.g. caused by oxidation and corrosion, as well as mechanical impacts, e.g. scratches and damage of coatings, are major factors that have to be considered. In this paper, we are demonstrating the investigation of mechanical damage of the coating and of the chemical composition of the metallic base materials used for two gilded medals that were issued on March 22, 1897, by Wilhelm II on the occasion of the 100th Birthday of his grandfather, Emperor Wilhelm I (1797 – 1888) [2]. It is known that about 1.2 million pieces of this Kaiser Wilhelm memorial medal also known as the Centenary Medal were struck. Although the medal was firstly issued in March 1897 and struck by Otto Oertel, several other manufacturers fabricated replicas of the gilded medals using different metallic base materials. In this paper, we are comparing two medals with similar appearance (see Figure 1). Mechanical damage of the gold coating, that was deposited using electroplating, is studied because scratches open the surface of the underneath base material, which can cause oxidation and corrosion. Since the kinetics of oxidation and corrosion of copper and copper alloys is determined by their composition, including trace elements, the chemical compositions of the two medals are determined. Since art objects that are on display in museums usually have to be characterized nondestructively, both destructive and nondestructive characterization techniques were applied and compared.



Figure 1. Images of the two studied medals: Front and back sites.

Experimental details

Both objects (medal A and medal B) have a similar appearance: these are gilded medals (diameter about 40 mm) with some scratches (signs of use). Scanning electron microscopy (SEM) images acquired at an acceleration voltage of 15 kV provide an information about the surface topology, and energy dispersive X-ray (EDX)

spectroscopy proofs that in some regions the gold coating has been entirely removed and the base

metal is visible (Figure 2). The thickness of the gold layer was measured for both medals. It is in the range of 200 ... 400 nm for both medals (Figure 3).

For the chemical analysis, the medals were mechanically cut, and the cross-sections were grinded, polished and finally cleaned with distilled water. The chemical composition of the objects was determined with EDX spectroscopy in the SEM and with X-ray fluorescence (XRF) spectroscopy using a portable tool (with Ag anode, operated at 50 kV and 200 µA).



Figure 2. EDX spectroscopy elemental map of Medal A (a) and Medal B (b) surface.



Figure 3. SEM secondary electron images: Topography of medal A (a) and medal B (b) surface and determination the thickness of the gold layer.

For trace element analysis, inductively coupled plasma mass spectrometry (ICP-MS) was used [3,4]. In this case the 25 mg of material was diluted in 5 mL of 65% HNO₃, 5 mL of H_2O_2 and 5 mL of H_2O at room temperature, and subsequently introduced into ICP-MS for the measurements. Table 1 summarizes characteristics of the analytical techniques used.

Results and discussion

For the characterization of the surface topology of art objects and of their chemical composition, it is preferable to start the investigation with nondestructive techniques, i.e. portable XRF or – if the object can be transported and is small enough – XRF and SEM / EDX in the laboratory. However, trace element analysis (e.g. using ICP- MS) is needed too, which is usually destructive and requires more efforts.

Table 2 summarizes the analytical results obtained for medals A and B. The chemical analysis shows that medal A consists of copper, zinc and tin as main elements (CuZn7Sn3 alloy), whereas medal B is made of low alloyed copper (Cu).

The p-XRF study, which is semi-quantitative because of the gold coating, confirms these values (CuZn6Sn4 and Cu). Based on the p-XRF data, small amounts of Pb (< 1 wt%), which are not homogeneously distributed in the materials, were found in both medals, and a small amount of Sb (< 1 wt%) in medal A (Fig. 4). ICP-MS data prove the presence of traces of Zn and Sn in medal B (< 0.1 wt%). Zn was quantified in the sample at the level of 0.016% \pm 0.002%.

Table 1. Characteristics of analytical techniques used to study the medals (LOD: limit of detection).

Method Tool		LOD	Obtained information	Limitations	
SEM/EDX (non- destructive for small objects)	MERLIN, Zeiss, Germany/ QUANTAX 400, Bruker, Germany	>10 ³ ppm (at cross- section)	Surface topology and chemical composition (near-surface region)	Inhomogeneity of the material, UHV, signal overlap	
ICP-MS (destructive, small sample volume)	NexION 3000D, Perkin Elmer, USA	110 ⁻³ ppm	Chemical composition, trace element analysis (bulk material)	Sample preparation, needs decomposition and transfer into solution	
p-XRF (non- destructive)	Niton XL3t GOLDD+. Thermo Scientific, USA	only qualitative results, because of gold coating	Chemical composition (bulk material)	Signal overlap	

Table 2. Elemental composition of medals: A and B by SEM/EDX.

		Medal A			Medal B		
	Series	wt%	а	at%	wt%	а	at%
Cu	К	88.7	2.8	88.8	98.5	3.0	96.5
Zn	К	6.8	0.3	6.6	-	-	-
Sn	L	3.3	0.1	1.8	-	-	-



Figure 4. p-XRF spectrum of the Cu alloy (medal A). Cu, Sn and Zn are detected, and in addition Pb and Sb as well as small traces of Fe and Ni. The Au lines result from the coating.

Conclusions

Two gilded Kaiser Wilhelm memorial medals with similar appearance were studied. Their chemical compositions are different: low alloyed Cu and CuZn7Sn3. The Cu-Zn-Sn alloy is a so-called red brass, i.e. a family of copper- based casting alloys containing 2-11 wt.-% tin and 1-10 wt.-% zinc, often with Pb as additional alloy element [5]. From these results we can conclude that medals A and B were manufactured differently, most probably in different mints. It can be assumed that one medal was an original struck by Otto Oertel in 1897, and the other one was a replica fabricated later by another manufacturer.

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Applications of a novel in-situ four-point bending device for materials analysis

P1.7

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In many industries, stress engineering plays an important role for the development of new products and materials. Microprocessors and microelectronic products for example are highly complex structures made from numerous materials with specific thermal and mechanical properties. Because of the different thermal expansion coefficients of the materials, mechanical stress occurs during manufacturing and use, which could result in fracture and failure of the products. Therefore, it is necessary to characterize these materials and also the influence of mechanical stress on the products. A common method to apply mechanical stress is loading components and test structures with the 4point bending (4PB) mode.

The advantage of 4PB is the constant bending moment between the inner support points. A novel rotational 4- point bending tool (rot4PB, Figure 1) for in-situ scanning electron microscopy (SEM) uses rotational sample clamps instead of standard fixed grip sets that are displaced towards each other in conventional tools. This enables a low building height for various applications while achieving high loads. The tool is designed for use in atmosphere in combination with additional analytical tools and for vacuum use, e.g. in SEM/FIB tools. Here, the unique working principle [1] allows various bending modes and alternating compressive and tensile stress on sample surfaces without changing the setup and without handling the sample outside the vacuum chamber. The mechanical stress on the sample surface can be determined at any point with the knowledge of the sample geometry through the measurement of the actual torque on both sample clamps.



Figure 1. Contact positions for a) compressive load and b) tensile load and a rendered visualization of the rot4PB tool.

The rot4PB tool can keep the bent state of a specimen due to a high holding moment even when powered off. This enables easy transfer in additional tools such as SEM/FIB, Raman spectroscopy, EBSD, nanoindentation, SPM and other techniques to study the sample surface of a specimen. Hence, it is possible to conduct indentation experiments on a bent specimen, transfer the setup from the nanoindenter tool to an SEM to investigate the indents in the SEM. This workflow was used to

p.36
investigate the crack length of indents on a thin film samples with an intrinsic compressive stress (Figure 2).



Figure 2. a) rot4PB tool in a Bruker TI950 nanoindenter for stress application on a bend sample. b) Mean values of the crack length and indent length of stressed and unstressed samples. c) SEM image of an indent on an unstressed sample and d) SEM image of an indent on a stressed sample with tensile stress horizontal direction.

Nanoindents were performed to calibrate FEM simulations where the fracture properties of the thin film were investigated. In these simulations the crack length must be greater than the indent length to get reasonable results. Without the application of additional tensile stress with the rot4PB tool the crack length was too small and did not meet this requirement [2]. The applied tensile stress was validated by Raman spectroscopy and correlates well with the internal calculation of the control software.

Conclusion

An in-situ rot4PB device was shown with novel applications, highlighting the possibility of linked experiments in various tools while maintaining the sample stress state.

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P1.8

A preliminary study on fabrication of diatomaceous earth/aluminium MMCs by spark plasma sintering technique

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Compared with composites, the possibilities to achieve an adequate combination of density, strength, toughness, or damping properties of monolithic metallic materials, are limited. Therefore, in the recent years, an increasing global demand for novel materials is observed. The market requirements led to rapid development of metal matrix composites (MMCs), which possess unique properties, often difficult to achieve in bulk metals and their alloys, e.g. high specific strength.

As a rule of a thumb, the functional properties of MMCs strongly depend not only on selection of the metallic matrix or processing route of a composite, but also on the size, shape, and amount of the added reinforcement phase. Currently, when developing novel MMCs, great attention is being paid to exploring the possibilities for using reinforcement materials of natural origin. For example, the sustainable sources of silica, which is often utilized in MMCs as a filler, are rice husk ash or wheat straws [1]. The advantage of using natural reinforcement materials in MMCs production is the possibility not only to obtain cheaper solutions, but also to responsibly manage waste from the agricultural industry.

Nowadays, the silica nano- and microparticles are often proposed as fillers for production of aluminium matrix composites (AMCs). Nevertheless, due to poor of wettability of silica-aluminium system [2], it is challenging to process the Al-SiO₂ mixture so that a composite of sufficient quality will be obtained. Therefore, up to date, various processing methods of those systems were introduced. For example, the SiO₂-reinforced AMCs are currently produced by powder metallurgy [3] or stir casting [4] methods.

In this study, a novel approach to producing SiO_2 -reinforced AMCs is proposed. As a matrix, pure aluminium was used, while the reinforcement – a natural ceramic filler material – consisted of food-grade diatomaceous earth (DE). Diatomaceous earth has a powder-like structure and consists of frustules – the three-dimensional, nanoscale- porous diatom cell walls, formed of silica. To our knowledge, DE-reinforced AMCs were not produced before.

For SPS sintering, four various mixtures of substrate powders (diatomaceous earth and aluminium) were prepared, with the following content of diatoms: 0, 10, and 30 vol. %. Commercial aluminium powder (grain size $44 \div 420 \mu$ m) was supplied by Alfa Aesar (Thermo Fisher GmbH, Germany), while diatomaceous earth was purchased from Perma Guard. Before consolidation, both substrates, in form of frustules and aluminium powders, were mixed in a mechanical stirrer for 1 h.

The AMCs were developed by the powder metallurgy route, using spark plasma sintering (SPS) technique. In SPS, pulsed AC or DC current directly passes through the graphite die, where the mixture of the substrates are placed. Therefore, in contrast to the conventional hot pressing, the heat is generated inside the die. Due to that, compared to conventional techniques of powder consolidation, remarkably high heating or cooling rates (up to 1000 K/min) are achieved. In this study, a HP-D-10

(FCT System GmbH, Germany) SPS system was used (Figure 1).



Figure 1. The SPS consolidating system: (A) an overview, (B) processing of a single sample.

For sintering, about 3 g of powder mixture was loaded into a graphite die (Ø10 mm), the internal surface of which was covered with a graphite foil sheet, to avoid direct contact between the powder compact and the graphite die. A summary of sintering parameters is given in Table 1.

Tabla 1	Paramotors of	the SDS	cintoring	procoss
Table 1.	Parameters of	the SPS	sintering	process

Series	Diatoms	volume	leating speed	Consolidation	sure/Force	Consolidation
	fraction		[°C/min]	temp.	[MPa]	time
	[vol. %]			[°C]		[min]
I	0, 10, 30		50	575	50	15
II	0, 10, 30		50	555	50	15

To assess the influence of DE content on the mechanical properties of Al composites, the small punch technique (SPT) was used. The tests were carried out using a Zwick/Roell Z005 universal testing machine, equipped with a 5kN load cell. For the deflection measurements, an electromechanical extensometer MTS 634-12F-25 was used.

For each sample, the force-deflection curves were collected. Based on the force-deflection curves, yielding force F_y , ultimate force F_u , as well as deflection at ultimate force A, were calculated. Moreover, using buoyancy method, density of the as-received samples was calculated. All samples were also subjected to scanning microscopy observations (SEM-FIB, Thermo Scientific Scios 2).

According to the results, SPS is a suitable method for Al-DE composites production. The best material quality, in terms of distribution of diatoms in the matrix, was achieved in samples obtained in series II. Moreover, the yielding force F_y was similar in all tested specimens, irrespective of the DE content. The ability of matrix to yield in DE-modified samples was confirmed also in SEM observations. On the other hand, as a result of diatom addition, the F_u of aluminium was substantially decreased. The achieved decrease in density did not compensate the significant drop in specific strength of the obtained composite materials.

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P1.9 The influence of capillary pores on transport of chloride ions – numerical simulations in nano-XCT based 3D cementitious microstructures

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The corrosion of reinforcing steel in concrete structures is a serious problem from the perspective of both safety and economy and affects directly the sustainability and life-time of the infrastructure. Corrosion of reinforcing steel is one of the most common degradation processes which can affect reinforced concrete structures causing their loss of serviceability, needs for repairs, premature pulling down, and in extreme cases can lead to structural collapse (e.g. the Genoa bridge collapse in 2019).

Concrete provides a highly alkaline electrolyte encapsulated in its pores, and in such conditions steel remains passive. However, chlorides and atmospheric carbon dioxide penetrate into the pores and promote corrosion when reaching the reinforcement, which weaken the concrete structural properties inducing the cover cracking and the loss in steel concrete bond. Chloride induced corrosion of reinforcing steel is one of the main causes of structural concrete deterioration, and therefore, it is responsible for a large share of the cost for the rehabilitation of concrete structures [1]. Since the concrete cover plays a crucial role in protecting the steel rebars, acting as a barrier for chlorides ingress, the durability of the concrete is a complex process with different parameters influencing the rate of penetration of ions. The most important one is the *effective diffusion coefficient*. It is defined based on the diffusion coefficient of the ions in a pure solution but it depends on the morphology of the porous material too. This morphology (microstructure) of the material is described quantitatively by *porosity* (ϕ), *tortuosity* (τ) and *constrictivity* (δ) parameters.

Simplified 1D models [2,3] neglect that concrete is a multiphase porous material with a 3D microstructure including channels (capillary and gel pores) for ionic transport. Therefore, we model ion transport in a real 3D cementitious material based on microstructure information from nano X-ray computed tomography (nano-XCT) measurements. A laboratory full-field transmission X-ray microscope (Xradia Ultra 100) was used at a photon energy of 8 keV with a field of view (FOV) of 65µm that provides a spatial resolution of sub-100 nm [4]. A small sample was carefully prepared without damaging it, to acquire image data within the FOV nondestructively. The tilt series for tomography covering an angular range of 180° consisted of 601 projections, with an exposure time of 110 s for each projection.



Figure 1. Visualization of cementitious material 3D microstructure determined based on the nano-XCT data and results of microstructure segmentation: cement (yellow), capillary pores (blue) and grains (grey and black). The diameter and the height of analysed sample is 52 μm.

One can distinguish four components in the 3D data of the studied material, determined from nano-XCT experiments: cement, capillary pores and two types of sand grains (Figure 1). The measured nano-XCT data was cropped to the smaller cylinder, 52 μ m in height and diameter. Then, the selected volume was subjected to the phase segmentation process, which was carried out by Simpleware Scan IP software. The cementitious material microstructure and the results of segmentation - cement (yellow), capillary pores (blue) and sand grains (greys) - are presented in the Figure 1. The phase segmentation was further used to create two different volumetric meshes for numerical simulations using the Simpleware FE module. Firstly, cement and capillary pores were treated as a single continuous phase, while subsequently, they were treated as the two different phases with separated meshes. The prepared 3D meshes were then imported into the COMSOL Multiphysics 5.4 software for numerical simulations.

Two models were applied to study the influence of capillary pores on the transport of chloride ions in cementitious materials. In both models, the sand grains were treated as a diffusion barriers, and thus they did not participate in the transport. In the first model, cement and capillary pores were treated as a single continuous porous phases, which is described by average properties, i.e. porosity. The chloride transport was described by the following equation:

φ

$$\frac{\partial c}{\partial t} = D_{app} \frac{\partial^2 c}{\partial x^2},$$
(1)

where: ϕ – the porosity of cementitious material, [%], c — the concentration of chloride ions [kg/m³], D_{app} — the apparent diffusion coefficient of chlorides ion in cementitious material [m²/s]. In the first model, we did not distinguish different types of the pores — cement was treated as a single continuous porous medium that consists of capillary pores, gel pores and solid particles.

In the second model, we distinguished capillary pores and gel pores, which were not visible considering the resolution of about 100 nm in the nano-XCT measurements. Thus, the chloride transport was described in two phases: The transport in capillary pores was described by eq. (2) and the transport in gel pores by eq.(3):

where: D_{in} — the intrinsic diffusion coefficient of chlorides ion in pore solution [m²/s], ϕeff – the gel porosity of [%], D_{eff} — the effective diffusion coefficient of chlorides ion in cement material with gel pores [m²/s]. The calculated chloride ion distribution in cement and in the capillary pores is presented in Fig. 2



Figure 2. Cement and capillary pores domains (left) created based on the nano-XCT measurements, used in the numerical simulations. An example of simulation results (right) — chloride ions distribution in cement and capillary pores.

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P1.10 Microstructure and mechanical behavior of fossil diatom frustules from Ellerbeckia and Melosira species

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Diatomaceous earth is a biogenic siliceous sedimentary rock, which mainly consists of fossil diatom frustules. Diatom frustules are potential materials for nanotechnology applications ^[1, 2], e.g. diatomite filters, diatom-based biosensing devices etc. In order to engineer the diatom material, their hierarchical microstructure and mechanical behavior need to be fully understood. Here, the hierarchical architectures of fossil diatom frustules (Genus from *Ellerbeckia* and *Melosira*) are studied by nano X-ray computed tomography (NanoXCT) ^[3, 4], transmission electron microscopy (TEM) and focus ion beam/scanning electron microscopy (FIB/SEM). In-situ micromechanical experiments with uniaxial loading were used to investigate the mechanical behavior.

With the quantitative study, the following microstructural dimensions and features are analyzed:

- (i) The surface and the inner structures of the selected frustules are obtained by nanoXCT.
- (ii) The size of ordered features on the round copulae of *Ellerbeckia* is measured at the unrolled cylinder wall.
- (iii) Structure information of the tube process and inter-valve face is acquired by FIB cutting and TEM with high spatial resolution.
- (iv) Element distributions of several important structure areas, i.e., tube process, center of the valve face, and the connection area of the epivalve and hypovalve, are obtained by energy-dispersive X-ray spectroscopy (EDX).
- (v) Nanopores of about 15 nm are revealed by TEM.
- (vi) There is the sealed layer structure on the valve inner face and connection area of the epivalve and hypovalve.

Here is the figure 1 to show the microstructures of *Ellerbeckia* imaged by nanoXCT.

In order to get the maximal loading force and the crack propagation behavior of these diatom frustules, uniaxial compression tests were performed in-situ in X-ray microscope on the surface of the valve face and on the copulae area. Analysis of the mechanical test reveals that the force and strain appear to be strongly dependent on the size of the frustules. The maximal force decreases as the cylinder diameter of the frustules decreases. For cylinder diameters of 80 μ m, 69.5 μ m, 62.5 μ m and 46 μ m, the corresponding maximal loading forces are 82 mN, 45 mN, 44 mN, and 20 mN, respectively. Furthermore, the cracking process of the diatom frustule is monitored by a series of radiographs. It is found that the crack initiates along the thinnest structure or the linkage structure (Fig.2). The tomographies were acquired before/after the compression test to elucidate the structure change before/after loading the force as well.



Figure 1. NanoXCT images of *Ellerbeckia*. The different structures of *Ellerbeckia* in valve view (a. b. d) and girdle view (c. e. f). Double directions blue arrow in (a): Diameter of this frustule is $60 \mu m$, red arrow head in (a, c): the frustule cell wall; red arrows in (b, e, f): tube processes from the surface to the inside; green arrows in (d, g): the valve face. (g) 3D rendering of the *Ellerbeckia*, orange arrow: Müller step.



Figure 2. Study of the mechanical behavior of *Ellerbeckia*. (a, b, c) 3D rendering of the frustule in different views (a: inner girdle view, b: outer girdle view, c: valve view) before compression test, (d) radiographs recorded during the mechanical test, (e, f, g) 3D rendering of the frustule in different views (a: inner girdle view, b: outer girdle view, c: valve view) after the compression test. Red line: crack propagation.

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P1.11 A combined soft and hard XPS study of the oxidation behaviour of postdeposition annealed titanium-tungsten diffusion barriers

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For high-power semiconductor devices, a binary alloy of titanium and tungsten (TiW) is often used as a diffusion barrier to isolate the copper metallisation interconnects from the silicon substructure. ¹⁻³ A diffusion barrier is necessary as copper rapidly diffuses into silicon at low temperatures (<200 °C), which can lead to premature device failure.

Despite the effectiveness of TiW diffusion barriers, a detailed characterisation study on the system has yet to be performed. Exposure to high temperature events, both experienced within the manufacturing route and during service can encourage the segregation of titanium out of the TiW alloy and into the copper.⁴ This mechanism can allow copper to bypass the barrier, leading to the formation of copper silicides which act as the epicenter of a host of thermo-mechanical failure mechanisms. Additionally, a commonly employed tactic to improve the copper blocking efficiency of the barrier is to expose the layer to air by a vacuum break, prior to copper deposition, which is thought to "decorate" the grain boundaries with oxides.³ Both this titanium diffusion mechanism and the oxidation behaviour of TiW are critical properties that have a direct influence on the performance and reliability of the device. In order to achieve improvements in these areas, TiW and its associated interactions must be better understood.

Here, un-patterned, Si/SiO2/TiW thin film stacks, with varying titanium concentrations and annealed for varying durations at 400 °C under an argon atmosphere were characterized using a combination of soft and hard X-ray photoelectron spectroscopy (SXPS and HAXPES). Combining SXPS and HAXPES provided the opportunity to study the chemistry across the TiW film both from a surface (< 5nm) and bulk (< 20 nm) perspective, respectively. Samples were annealed to study the titanium diffusion mechanism and in parallel, the same samples were left exposed to the ambient environment to study the oxidation behaviour.

Results showed that an increase in the titanium concentration was observed at the surface with increasing annealing duration. An increase of up to 17 at.% in the titanium signal was observed after only 0.5 h of annealing, highlighting the severity and speed of this diffusion mechanism. The accumulation of titanium at the surface, accelerated the rate of oxidation due to the high chemical affinity of titanium to oxygen. Full metal to oxide conversion was not observed in either case of titanium or tungsten and metallic features were still retained. Multiple titanium and tungsten states were also observed but the rate of titanium oxidation was significantly higher than tungsten. This combinatorial characterisation approach worked well as the respective techniques complemented each other's shortcoming. Additionally, the results provided a detailed account on the oxidation behaviour of the TiW interface, which will be directly fed back to industry, optimizing future device technologies.

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P1.12 Small Amphiphilic Ligand-based Synthesis of Hydroxyapatite Nanoparticle for Titanium Implant Coating: Characterization& Analysis

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Titanium prosthetics are commonly used devices in orthopedics and craniofacial surgery applications. Coating of orthopedic titanium implants with biocompatible hydroxyapatite nanoparticle (HANP) is a promising approach to facilitate bone cells anchorage and osteointegration. Herein, we report synthesis of hydroxyapatite nanoparticle (HANP) in presence of a malonic acid amphiphile (MA) through biomineralization approach and its coating onto titanium implant for potential bone tissue engineering application. HANPs synthesized by in situ precipitation were subjected to FTIR analysis, wherein the characteristic peaks at 3568, 1461, and 1041 cm-1 were observed. In PXRD analysis, the prominent peaks at around 2? = 26° and 2? = 33° indicated MA-mediated generation of hydroxyapatite phase. FESEM and FETEM analysis revealed that HANPs were spherical-shaped and 22-27 nm in size. HRTEM indicated that the lattice distance for HANPs was 0.29 nm, while the crystallinity of HANPs was validated by SAED. TGA indicated degradation of HANPs from 20°C to 800°C, with 87% residual mass, while BET analysis revealed that HANPs had a surface area of 90 m²/g and an average pore size of 4.04 nm. The surface of titanium (Ti) wire was coated with type-I collagen and HANPs (1mg/ml concentration) and characterized by FESEM-EDX and FTIR analysis. FESEM analysis revealed a homogeneous appearance of HANPs deposited onto the surface of Ti wire. Subsequently, EDX analysis confirmed the presence of Ca, P and O elements. FTIR analysis revealed the presence of characteristics peaks of HANPs in case of coated titanium wire. The HANP synthesized by malonic acid amphiphile was non-toxic to cultured MG-63 osteosarcoma cells. Proliferation of MG-63 cells over HANP-coated Ti wire was evidenced by resazurin assay and calcein-AM staining. An increase in alkaline phosphatase activity and enhanced expression of collagen I (Col-I), alkaline phosphatase (ALP), Runt-related transcription factor 2 (Runx2) and osteocalcin (OCN) osteogenic differentiation markers was noted for MG-63 cells growing on HANPcoated Ti wire. In addition, alizarin red S staining indicated calcium mineral formation. It is envisaged that malonic acid amphiphile-mediated synthesis of HANP outlined herein holds interesting prospect to generate biocompatible nanomaterial-coated Ti wire implant for bone tissue engineering applications.

P1.13 Gold-coated silicon nanowire arrays for molecular sensing using surfaceenhanced Raman spectroscopy

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It is shown that silicon nanostructures can be used as a template for the creation of gold nanostructures of various morphologies. These nanostructures are used as surface-enhanced Raman scattering (SERS) sensors. The SERS activity and the chemical stability of gold (Au) allows the Au@Si substrate to possess perfect sensitivity, homogeneity, reproducibility and chemical stability. Here the silicon nanowires matrix (SiNWs) was obtained by the use of metalassisted chemical etching (MACE) of boron-doped single crystalline Si wafer. For the formation of Au nanoparticles (Au NPs) the SiNWs was immersed in AuCl3 and HF solution as described in [1, 2]. The resulting samples were examined using Carl Zeiss ULTRA 55 FE-SEM scanning electron (SEM) microscopy and Confotec ™ MR350 confocal Raman microspectroscopy. The resulting SEM image clearly shows Au NPs are about 100 nm located on SiNWs. The samples were used for detection 4-mercaptopyridine (4-MPy) in different concentrations. The possibility of diagnosing 4-MPy up to a concentration of 1 nM has been demonstrated.

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P1.14 Nano-mechanical and nano-tribological investigation of metallic and carbonitride TiCrCoNiV high entropy alloys

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During the last years, the high entropy alloys (HEAs) have attracted more attention than conventional alloys due to their improved strength, mechanical properties even at elevated temperatures, oxidation resistance, ductility and fracture toughness. In this study, machine and automotive industry was targeted, where medium-to-high friction and wear resistant coatings are needed. For this purpose, coatings of metallic and carbo-nitride TiCrCoNiV high entropy alloys were developed by a hybrid technique consisting on magnetron co-sputtering of high purity elemental targets in inert and reactive atmospheres of Ar and Ar CH4 N2. A con-focal magnetron sputtering system was used, AJA ATC-ORION, equipped with five unbalanced magnetrons fed by HiPIMS (Cr target), DC (Ti and V targets) and RF (Co and Ni target) sources. The coatings were investigated in terms of elemental and phase composition, morphology, density and roughness by EDS, XRD, AFM, XRR. Moreover, a mechanical behaviour at micro and nano scale was performed. Nanoindentation was carried out by measuring the load-displacement curves characteristic to each deposition type. Hardness (H) and reduced modulus (Er) were obtained by using a maximum indentation load of 6 mN. Adhesion was evaluated by progressive load scratch test and critical load for each deposition was determined. Further, multi-pass scratch test was used to evaluate wear behaviour at subcritical loads. Surface profilometry, used to assess the coatings thickness, showed a media of about 2.5 μ m. The metallic HEA coatings showed an increased friction coefficient of about 0.35 at an applied force of 1 mN, while the carbon richest carbo-nitride HEA showed the largest values of H (18.0 GPa) and Er (213.4 GPa). The highest adhesion and the calculated wear rate (obtained after 10 passes by applying 2 N constant load) were exhibited by the metallic coating.

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P1.15 Preparation and investigation of plasmonic properties of Ag/Au alloys

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Different concentrations of Ag/Au alloys were synthesized using 'green chemistry' approach. The aim of the study was to determine the appropriate concentration of Au that provides protection against oxidation for the silver nanoparticles, while maintaining the enhanced plasmon properties of the latter. We started from two liquid solutions containing: (a) Au nanoparticles (commercially available under the name Bright Brushing Gold[®]) and (b) Ag extracted in lavandin oil from silver conducting paste. The two solutions were mixed in different proportions in order to obtain three types of alloys: (1) 20%-Ag:80%-Au; (2) 40%-Ag:60%-Au and (3) 50%-Ag:50%-Au. The solutions were thermally treated at 12000C and at 1800C. The resulting deposit was investigated using SEM, EDX and Raman spectroscopy.

Keywords:

silver-gold alloy, plasmonic properties, surface enhanced Raman scattering, green chemistry

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Microstructure and catalytic activity of Al13Co4 melt spun alloy

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Intermetallic compounds are promising materials in many application areas [1]. Due to their unique structural properties, these alloys show catalytic properties that can be applied for various chemical transformations. The development of catalysts based on intermetallic compounds may limit the use of noble metals for this purpose. Catalytic properties of intermetallic phases result from the presence of active centres that are atoms of the transition metal distributed in well defined structure. One of quick developing groups of materials are phases based on aluminium. Implementing these materials for industrial applications would benefit from the low cost and wide availability of the constituent metals [1,2]. Al13TM4 (TM- transition metal) compounds, which are also approximants of decagonal quasicrystals, are phases of interest because of various inequivalent adsorption sites and a chemical bond network that provides segregation resistance and structural stability [3]. The atoms arrangement causes site isolation, which ensures the presence of electronic and geometric effects responsible for high activity and selectivity of the catalyst. Previous studies confirm the possibility of use cobalt and iron as a transition metal with encouraging result. The phases based on these metals have high selectivity in reactions of semihydrogenation of unsaturated hydrocarbons [4]. Preparation of materials of quasicrystal approximant structure is exigent due to the narrow compositional range of these phases in Al-Co system and segregation of its components [5]. To avoid such difficulties rapid solidification methods are used. In the present work the melt spinning method was proposed. This technique of production intermetallic phases has not been widely used so far, so the aim of this study is to examine the microstructure of the obtained ribbons and testing of their catalytic properties. The Al75.8Co24.2 (in at. %) ribbons, corresponding to Al13Co4 phase have been produced by melt-spinning technique. The ribbons were obtained in the form of fragmented, brittle flakes. Heat treatment was carried out to obtain a single-phase structure. The ribbons were annealed at 900 °C for 78 h. Thin foils were prepared for as spun ribbon flakes and after annealing. The microstructure of the ribbon was examined using FEI scanning electron microscope (SEM) E-SEM XL30 and FEI transmission electron microscope (TEM) Tecnai G2. Catalytic properties tests were carried out by hydrogenation of phenylacetylene reaction, a model process for the selective hydrogenation of alkynes to alkenes, in an agitated batch glass reactor. A gas chromatograph (Clarius 500, Perkin Elmer) with He as a carrier gas was used for analysing the reaction mixture. The SEM micrograph of the cross-section of the as spun Al13Co4 ribbon revealed the columnar structure resulting from directional solidification in the examined material in direct contact with the rotating drum, which contains the elongated grains with the second phase located between them. More uniform grains were observed near the free surface of the ribbon due to the reduced cooling rate in this region. The microstructure observed by TEM confirms the presence of two phases: dark grains containing 74 at.% of Al and 26 at.% of Co and light regions enriched in aluminium, with average composition 83 at.% of Al and 17 at.% of Co. The selected area diffraction patterns (SADP) allowed to identify the crystal structure of the observed phases. It was found that the grains correspond to the quasicrystalline phase. Similar structures of decagonal quasicrystal were observed in the Al-Co alloys by Ma [6]. The area between the grains was identified as monoclinic Al9Co2 phase (space group P21/c and lattice parameters a=0.6216 nm, b=0.6288 nm, c=0.8559 nm, ?=94.77°). Annealing at 900 °C for 78 h caused the transformation to a single-phase structure of the grains composed of Al77Co23. Based on the SADP?s these grains were identified as orthorhombic Al13Co4 phase (space group Pnm21, a=0.8158 nm, b=1.2342 nm, c=1.4452 nm). The characteristic for this phase stacking faults are visible inside all grains. In the catalytic tests the Al13Co4 intermetallic compound was used in both forms, as received and after annealing. Before the experiment the flakes were pulverized in a vibration ball mill and sieved to separate powder fractions. For catalytic tests the fraction below 32 ?m was selected to increase the active surface area. All the ribbons catalyse the hydrogenation reaction with different conversion rate and selectivity depending on the microstructure and process conditions. It was found that for annealed ribbons with single-phase structure better results of the catalytic reaction than in as spun state were registered. A higher degree of conversion for both states of material was achieved at 60 °C. The highest degree of conversion 31% was obtained for annealed Al13Co4 at 60°C and the highest selectivity to styrene was registered for annealed ribbon at 25°C. Rapid solidification and annealing enabled obtaining single-phase orthorhombic Al13Co4 structure, which provide higher catalytic performance than multiphase material. Further investigation will be focused on the enlargement of specific surface area. It should improve the activity of catalyst and increase the degree of conversion in the reaction.

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P2.2 Microstructure and phase composition of refractory ceramic shielding thermally exposed parts in steel making process

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Recycling of refractory ceramics is gaining momentum given environmental concerns due to industrial waste accumulation as well as dwindling supplies of refractory raw materials. It thus become crucial to develop strategies allowing for ceramic waste to re-enter the industrial circle (circular economy). Some limitations for reusability of spent ceramics are imposed nonetheless by the extent of mineralogical damage, e.g. contamination with slag, partial infiltration with steel, increased fraction of low density volatile hard to sinter powders, typically accompanying the industrial on-site steel making processes. Therefore, the elaboration of any new recycling strategy of the industrial ceramic waste requires a detail estimate of the reusability of such materials including their microstructure and phase composition assessment. However, analysis of this multi-component ceramic pose a challenge for scanning electron microscopy due to low contrast differences between respective phases and excessive charging. Thus, in this work a low voltage scanning electron microscopy is implemented for the characterization of the spent refractory pastes. Few stages of the industrial process are reconstructed on the laboratory scale to pin point the phase evolution. The performed investigations helped to acquire a set of preliminary data needed for development of a feasible technology of ceramic waste recycling.

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P2.3 Influence of W addition on microstructure and properties of TiB₂-W coatings

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Technical development is closely related to the development of knowledge in the design, production, and processing of new material functions [1]. Particularly intensive development concerns new materials in the areas of the automotive industry [2] and aviation [3], but mostly in the tool industry [4]. Advanced solutions for the production of thin anti-wear coatings are of great importance. New anti-wear coatings are to enable modification of functional properties of machine and tool parts, thanks to which they can operate in increasingly difficult conditions, e.g. high mechanical and thermal loads, intensive wear, or harmful corrosive environment. Currently, extensive research is being carried out on ultra-hard thin anti-wear coatings [5-8]. Titanium diboride TiB₂ is characterized by high hardness, Young's modulus [9] and high thermal conductivity [10], as well as high chemical resistance [11] and thermal resistance [12]. TiB₂ coating is characterized by a very low affinity to aluminium [13], which indicates that it can be a good anti-wear agent as a cutting tool material for machining aluminium alloys. However, despite very interesting properties of the coating, TiB₂ has not found a wide commercial application due to very high brittleness caused by a high state of the inherent stress.

The aim of this work was to investigate the influence of doping TiB_2 coatings by tungsten on structure and properties. TiB_2 coatings with various W contents (0, 3, 6, 10%) were fabricated using the magnetron sputtering method from TiB_2 and W targets.

The chemical and phase composition, microstructure, and mechanical properties, were investigated using different techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) with analysis EDS and nanohardness.

The results showed that the microstructure of the W-TiB₂ coating change with doping by W. With an increase of contents W decreases the crystalline size and the preferential orientation is visible. TEM analysis indicated the nanocrystalline columnar structure witch change also with tungsten contents. In coating with W =3, 6% we observed only TiB₂ grains encapsulated by a region rich in tungsten. In coating with 10% W, the structure reminds nanocomposite Ti-B-W.

The nanohardness increases with growth of doping W. The change in hardness is also manifested in the observations of cracks around the place after the indenter Berkovich (Fig. 1.).





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P2.4 Generating new excitation pathways for green emission of InGaN/GaN MQWs by Xe swift heavy ion irradiation

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III- nitrides are wide bandgap semiconductors mainly used in optoelectronics and high-power electronics. Currently, blue InGaN/GaN light emitters are well-established with efficiencies up to ~80%. However, their efficiency is known to decrease with increasing emission wavelength due to polarization effects and Auger losses. The introduction of In compositional gradient in InGaN/GaN multi quantum wells (MQWs) is expected to reduce these effects, and therefore improve the efficiency of III-nitride emitters.¹

Swift heavy ions (SHI) are high energy (above ~1 MeV per nucleon) ions that lose their energy mainly by electronic excitations instead of elastic collisions when passing through the material. Thus, SHI irradiation may be a potential solution to achieve intermixing in MQWs with a reduced density of lattice defects usually generated by low-energy ion irradiation. In this work, the effect of SHI irradiation on the optical properties of InGaN/GaN MQWs is studied.

InGaN/GaN MQWs (barrier: 11nm, 5× periods: 13.7 nm) grown by metalorganic vapor phase epitaxy (MOVPE) on GaN on sapphire were irradiated with 92 MeV ¹²⁹Xe SHI (fluence: 2×10^{12} cm⁻²). In order to understand the impact of the ions' energy on the MQWs, Al foils with different thicknesses were placed in front of the beam to reduce its energy from 80 MeV (Al thickness: 0.8 µm; energy loss at the surface (SES): 21.1 keV/nm) to 36 MeV (Al thickness: 5 µm; SES: 12.6 keV/nm). These values are above and below the reported threshold value for the formation of ion tracks in GaN (~15 keV/nm).² As a reference, GaN layers grown on sapphire were also irradiated under the same experimental conditions. The samples were studied by optical spectroscopy techniques: transmission, micro-Raman, photoluminescence (PL), and PL excitation (PLE).

It is found that Xe SHI irradiation generates crystal damage, evidenced by i) the activation of the GaN phonon density of states (DOS), Figure 1 (a), and ii) a redshifted and less abrupt GaN near band edge response in the transmission spectra. This behaviour is similar in GaN and InGaN/GaN MQWs. Indeed, an absorption band (peak at ~450 nm) is generated after irradiation for both structures. By exciting through this band, no PL emission is obtained for GaN in the studied spectral range, while it is achieved for MQWs. This resonant electronic state, related to InGaN, is also involved in the Raman scattering process, where an increase of the $I_{A_1}LO$ (I_{InGaN})/ $I_{E_2}H$ (GaN) ratio and the 2LO phonon (InGaN) is observed in Figure 1 (a). Independently on the SHI energy, a green emission is obtained for the MQWs using the excitation at 460 nm as illustrated in Figure 1 (b). Furthermore, it is important to note that the green emission is no more excited through the GaN NBE after the Xe SHI irradiation.

In conclusion, Xe SHI irradiation affects both GaN layers and InGaN/GaN MQWs damaging their crystalline structure. However, for MQWs an electronic state involved in the excitation of the green emission is created, showing the possibility to obtain that emission with lower excitation energy after



Figure 1. (a) Room-temperature Raman spectra dependence on SHI energy and (b) PL and PLE spectra of the as-grown and SHI irradiated (AI thickness: 1.5 μm) MQWs.

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P2.5 Microstructure investigation of silicon nitride-zirconia-graphene composite using multi-scale microscopy

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Materials used at high temperature often require good mechanical properties (e.g., fracture toughness, bending strength, etc.), good resistance to thermal shock, creep resistance, high thermal conductivity, good tribological and wear properties ^[1-4]. Ceramic materials have been extensively investigated in previous decades due to their high temperature performance in general. As one of the most promising candidates of structural ceramics, silicon nitride (Si₃N₄) meets the requirements mentioned above (e.g., low coefficient of thermal expansion (CTE), good thermal conductivity and high strength results in a higher thermal shock resistance than most other ceramic materials). Therefore it is commonly used in a variety of structural applications such as cutting tools, pump seal parts, bearing balls, gas turbine engine parts or heat exchangers ^[5-7]. Typical metal oxides (e.g., MgO, Al₂O₃, Y₂O₃, or ZrO₂) in Si₃N₄ promote a liquid phase formation, which facilitates the consolidation ^[4]. Due to the unique combination of electrical, thermal and mechanical properties ^[8], graphene and graphene oxide (GO) have been considered as filling component in ceramic composites in the last decade. Although using either ZrO₂ or graphene nanofiller to improve the properties of Si₃N₄ has been reported, the study on the combined effect by both is rather rare.

Silicon nitride-zirconia-graphene composites with high graphene content (5 wt% and 30 wt%) were sintered by gas pressure sintering (GPS) in this study. The effect of multilayer graphene (MLG) content on microstructure is investigated by multi-scale microscopy. Multi-scale microscopy confirms that the phases disperse evenly in the microstructure without obvious agglomeration. The size distribution of Si₃N₄ phase shifts towards a larger size range with the increase of graphene content from 5 wt% to 30 wt%, while a higher graphene content (30 wt%) hinders the growth of ZrO₂ phase. MLG flakes well dispersed between ceramic matrix grains can slow down the phase transformation from α to β -Si₃N₄, subsequent needle like growth of β -Si₃N₄ rods and the densification due to the reduction of the sintering additives particularly in the case with 30 wt% MLG. Since MLG fillers in Si₃N₄- ZrO₂ ceramics makes the densification of composites more difficult, high porosity up to 50% is observed. Highly heterogeneous ceramic composite with shear-weak graphene and high porosity results in considerable redistribution of stresses under indentation. This type of dispersed damage caused by significant redistributed stresses prevents the formation of long macro cracks (classical radial cracks), which often occur in homogenous Si₃N₄ ceramic. Therefore, both of the Si₃N₄/MLG composites show resistance to contact or indentation damage.

Figure 1 shows two extracted slices from a volumetric reconstruction of X-ray computed tomography data. The square pillar sample was prepared from the synthesized composite with 30 wt% MLG using focused ion beam (FIB) milling in a scanning electron microscope. The 3D microstructure study using X-ray microscopy (XRM) was performed at synchrotron source (BESSY II, U41-PGM1-XM beamline ^[9]). ZrO₂ phases could be easily differentiated by the contrast, while only partial Si₃N₄ phases could be distinguished from mixed Si₃N₄ phase and MLG flakes. The phases are dispersed homogenously in the 3D microstructure, no obvious agglomeration of phases was observed.



Figure 1. Extracted slices from a volumetric reconstruction of the composite with 30 wt% MLG by synchrotron X-ray tomography. ZrO₂ phases are indicated by blue arrows, Si₃N₄ phases are indicated by red arrows.

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P2.6 ZnO low-dimensional nanostructured porous thin films for photocatalytic degradation of methylene blue in water purification

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Zinc oxide (ZnO) is one of the most common transparent conductive oxide (TCO), having unique properties, such as wide band gap of 3.37 eV, high electrical conductivity (\sim 102 ?-1·cm-1), large binding energy (60meV), combined with high charge carrier mobility. This is why it has found wide application in different fields, mainly in microelectronics, including gas sensor devices, photodiodes, flat-panel displays, and solar cells [1-4]. Moreover, ZnO - in the form of low dimensional nanostructures - exhibits an interesting photocatalytic activity, which can be applied in the effective UV-light activated photocatalytic degradation of different types of dyes - such as methylene blue (MB) - in the process of water purification[5,6]. In this work, the ability of ZnO nanostructures to photocatalytically degrade MB in aqueous solution was investigated: these nanostructured ZnO porous thin films were deposited by direct current reactive sputtering (DCRS) on the Si substrates [7-9]. To study the mechanism of MB photocatalytic degradation in depth, surface morphology and surface chemistry of these nanostructured ZnO porous thin films were assessed using complementary techniques such as Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS). The photodegradation of MB was performed illuminating the samples with an irradiance of ~ 2.0 mWcm-2. The degradation reaction (removal) of MB in aqueous solution upon UV irradiation was followed by spectrophotometric measurements. The observed absorption decay followed a zero-order kinetics [10] and was fitted using the following equation: [?]! = ?? ? ? + [?]" where [A]t is the concentration of MB at irradiation time t, [A]0the initial concentration of MB, k the zero-order rate constant, and t their radiation time. This kinetic behaviour is typical of degradation occurring with immobilised photocatalysts. The obtained results were interpreted on the basis of the information on the surface properties and the relevant photocatalytic properties of ZnO nanostructured porous thin films: their surface morphology was studied together with the surface chemistry, which revealed the adsorption of various undesired gases present in the atmosphere and other contaminants dissolved in water, as determined by using XPS and AFM methods. Finally, our studies confirmed that properly selected ZnO nanostructures can be very efficient for the photocatalytic degradation of MB in water purification, which paves the way for the utilization of these nanomaterials for environmental remediation purposes.

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P2.7 Preparation of nanoceramic materials and composites by needleless electrospinning

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A number of oxide ceramic materials such as alumina, titanium, tin, and zirconium dioxides and others are widely used as refractories, sensitive elements of sensors, catalysts, photocatalysts in dyesensitized solar cells and water treatment. Due to the unique properties of nanofibers, such as high surface-area-to-volume ratio, porosity, mechanical strength, these materials in nanofibrous form show better characteristics and are used in advanced composite materials.

The presented work aims to study the application potential of the solution-based needle-less electrospinning, performed on the Nanospider NS Lab200 machine, as a perspective technique for nanofibrous materials preparation. The main focus of the study was made on the preparation of the precursor fibrous materials and its transformation into special ceramic ones. This was performed based on a titanium dioxide (TiO₂) system. The fabrication process consisted of three basic steps: 1) preparation of spinning solution; 2) electrospinning; 3) post-spinning treatment. For spinning solutions preparation polyvinylpyrrolidone (PVP), titanium tetraisopropoxide, ethanol, and acetic acid were used. Prepared precursor fibers were used to study the influence of the post-spinning treatment type - conventional heat or low-temperature plasma treatment, and its conditions on the composition, morphology, and properties of the final fibrous materials, obtained from the same precursor fibers. The post-spinning treatment is the key step for the transformation of electrospun precursor fibers to oxide or non-oxide ceramic, carbon, and polymer-based composite fibrous materials.

Titanium dioxide was chosen due to the multifunctional nature and possibility of simple transformation into non- oxide ceramics, which allows being used further as the model system for the preparation and study of fibrous ultra-high temperature ceramics. As a result (Figure 1), after the calcination of the electrospun precursor in air, a series of titanium oxide nano/microfibers with different anatase to rutile phase ratio was obtained. In the case of the heat treatment experiments in the inert argon atmosphere – the carbothermal reduction took place and composite carbon/titanium oxides and titanium carbide fibers were obtained [1].

The same electrospun precursor fibers were treated by low-temperature plasma-induced surface sintering process by a special dielectric barrier discharge, so-called, Diffuse Coplanar Surface Barrier Discharge (DCSBD). Plasma treatment of the prepared samples was performed in three different by nature atmospheres: oxidative – air, reductive – H_2 , and inert – N_2 . The exposure times were 10, 30, and 60 min at the input power of 400 W. Impact of the plasma treatment time in different atmospheres on the morphology and chemical composition of the PVP/TiO₂ microfiber mats was studied. This type of treatment led to the formation of flexible composite TiO₂/PVP core/shell fibers. It was found that a thin ceramic layer was formed on the surface of the fibers, thickness, and morphology of which depends directly on the exposure time and atmosphere. One of the main aims of this work was to compare the impact of plasma treatment in the atmosphere with different chemical nature on the same composite system [2].

For the comprehensive structural and chemical study of the prepared materials electron microscopy

coupled with energy-dispersive X-ray spectroscopy (SEM/EDS, TEM), differential thermal analysis, differential scanning calorimetry coupled with thermogravimetry (DTA, DSC/TG), X-ray diffraction (XRD), and small-angle X-ray scattering (SAXS), ultraviolet-visible (UV-Vis), Fourier-transform infrared (FTIR), Raman, and X-ray photoelectron (XPS) spectroscopies were used.



Figure 1. Variety of materials obtained from the same precursor PVP/TiO₂ microfibers.

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P2.8 Diatoms' frustules as a possible natural filler in composite materials

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Diatoms are the largest and the ecologically most significant group of organisms on Earth. Due to the unique silicified cell structure as well as intricate morphology, these microorganisms attract scientists attention for a long time. Nevertheless, discussions about the details of their structure as well as functionalities, between scientists from various science fields, are still ongoing. Nowadays, possible applications of these diatoms shells are the subject of many works. The variety of the species makes it possible to choose frustule with desired structure, size as well as other parameters. One of the species of Authors' interest is freshwater diatom - Didymosphenia geminata. In addition to siliceous cells, Didymosphenia geminata secretes extracellular polymeric fibrous material in form of stalks. These stalks are responsible for attachment to substrates, like stones, plants, debris. The current studies allowed to conduct several investigations which allow to obtain comprehensive information's about siliceous shells. In addition to that, preliminary results of the possibilities of using frustules of this diatoms as a novel filler in epoxy composites have been presented in [1,2].

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P2.9 A novel approach to evaluate mechanical BEoL stack stability utilizing Cupillar shear-off and acoustic emission

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In this work, a novel approach is presented to identify and evaluate the occurring damage in BEoL (Back End of Line) stacks under mechanical load. The measurement strategy is firstly applied to evaluate the mechanical stability in the BEoL stack of copper (Cu) pillar bumped chips manufactured in 28 nm technology. In the measurement workflow, shear force is applied to a single Cu-pillar utilizing a tribo indenter system with a customized tip. The sample is placed in a special sample holder directly on top of a piezo-based acoustic emission (AE) sensor. While shearing off the pillar, acoustic signals are measured which are caused by damage events inside the BEoL stack and can be used to determine the exact moment and evaluate the type of damage. The results of the acoustic emission measurements are a valuable additional information to the mechanical data generated by the tribo indenter system. In combination with the damage visualization by e.g. light microscopy, it provides a more holistic insight to the damage infliction and propagation process in the BEoL stack and enables the identification of critical damage prone areas.

Keywords - Back End of Line stack stability; Chip Package Interaction; Acoustic Emission, Cu-Pillar Shear-Off, Advanced Packaging

Introduction

In the field of automotive and especially in the case of automated driving, higher requirements must be fulfilled for semiconductor devices compared to e.g. consumer products. This is due to the safety demands and the harsh environmental conditions. The extended reliability needs require a more robust design and specific testing and qualification procedures which is very time consuming. This sets a high demand for new metrology approaches to accelerate the testing procedures. An optimized approach would substitute e.g. the time-consuming temperature- based through pure mechanical testing.

Mechanical BEoL stack stability evaluation

It is attempted to apply such a pure mechanical testing approach to evaluate the stability of the BEoL stack as well as the interface between solder joint and the subjacent BEoL. This can be done on chip level by applying load to respective single solder joints (SnAg bumps or Cu-pillar) and analyzing the failure conditions and resulting damage. For SnAg bumps this can be done in accordance with the JEDEC standard JESD22-B117B [1]. However, there is no such standard yet for advanced packaging using Cu-pillars. A first approach for Cu-pillars is the so- called bump assisted BEoL stability indentation (BABSI) test [2]. This is a two-step process in which a Cu-pillar is first indented and then sheared off. However, this does not work if the Cu-pillar is capped with a solder material due to the plasticity of the latter.

Besides the damage infliction procedure also the question of damage propagation analysis must be taken into consideration. In case of [1] and [2] the shear force as well as imaging are the main evaluation methods for the occurring damages. In this work, a new approach is introduced that additionally utilizes acoustic emission (AE) measurements as a damage indicator and, to a certain extent, as a damage classifier. AE is already widely used for structural health monitoring (SHM) in e.g. airplanes, wind turbines, and gas tanks. It has also been shown in previous works that AE can be used to measure damage occurrence in specific thin films used in semiconductor manufacturing [3]

Test vehicle and developed experimental approach

The test vehicle used was an SRAM chip manufactured by GLOBALFOUNDRIES in 28 nm technology bumped with 100 μ m diameter Cu-pillars (Fig. 1a). A specific holder for the sample as well as the AE sensor was designed to conduct the experiments inside the tribo indenter system. Also, a customized indenter tip, a sharp shear knife, was used for the Cu-pillar shear-off (Fig. 1b). Using this setup, the optimal shear parameters were determined.

A displacement-controlled shear experiment with a constant shear velocity of 5 µm/s was conducted with the occurring force being constantly measured. The AE measurement with a sample rate of 100 MHz is triggered by the first acoustic event. The shear off typically occurs at around 500 mN for the used sample and triggers an acoustic burst event (Fig. 1c). This type of AE event indicates that a sudden structural change appears and not e.g. a plastic deformation. Compared to the mechanical signal the AE signal has a much higher temporal resolution and hence reveals that the damage induction process consists of several sub-processes (Fig. 1c). After the shear- off of the Cu-pillar, the damage can be evaluated e.g. utilizing 3D-light microscopy (Fig. 1d). Analyzing the visualization, the different stacks through which the damage propagated can be identified.



Figure 1. Test vehicle (a), schematic depiction of experimental setup (b), Force progression over time (orange) and occurring AE signal (blue) during shear off (c), and resulting damage with shear direction (d)

Conclusions and Outlook

In this work, it could be shown that acoustic emission is a suitable technique to identify the damage occurrence in BEoL stacks under mechanical load. The acoustic damage indication is more precise than for the lateral force measurements which means that even small damages which cannot be measured with a tribo indenter system can be detected. Further information regarding the damage can be derived from the shape of the AE signal. These factors suggest that AE measurements are an auspicious additional technique to identify and evaluate the occurrence of damage in a BEoL stack under mechanical load.

However, conducting a detailed damage evaluation utilizing the AE signal is challenging. Therefore, the developed workflow will be refined. Shear experiments with step-by-step loading in the sub-critical regime will be carried out. It will be halted once a damage is detected acoustically. This initial damage will then be analyzed to obtain a further understanding of the cracking initiation and propagation characteristics in the BEoL stack.

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P2.10 Structural and Electronic Effects of X-ray Radiation on Prototypical Catalysts

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X-rays are essential in a wide variety of advanced characterisation techniques to probe properties of matter. However, interactions of X-rays with crystalline matter are known to induce a range of changes. Despite the undesirable consequences of radiation being well documented in biological macromolecular crystallography since it was first studied in the 1960s[1,2], knowledge of the effect of this ionising radiation on small molecular crystals, which are integral in catalytic applications for instance, remains incredibly limited. In recent years the advent of modern microfocused laboratory sources and the shift towards higher brilliance synchrotron sources has exacerbated the problem of unwanted radiation effects, increasing the necessity for a better understanding of its influence on matter. The main aims of observing changes caused by irradiation are not only to design and implement preventative measures but also to fully understand the radiation damage process and how it occurs in the materials being studied. In this study, a combined approach of synchrotron (Diamond Light Source) powder X-ray diffraction (XRD) with X-ray Photoelectron Spectroscopy (XPS) is implemented to infer changes to the structure and to the local chemical environments, as well as changes to the electronic structure of a family of prototypical catalysts. These have the general formula [M(COD)X]2 where M= Ir, Rh, COD= cyclooctadiene and X= Cl. Approaching radiation effects with this combination of advanced techniques allows for a compelling, novel multi-modal way to probe effects of X-ray irradiation, by way of a direct correlation of structural changes with changes of the chemical state of the metal. The progression of radiation-induced changes to these small molecular crystals is monitored over considerable timescales and observations from experiments are complemented with theoretical results from Density Functional Theory (DFT) calculations. Insights into the structural implications of probing the sample at the high resolution I11 PXRD beamline at Diamond Light Source are obtained from Le Bail refinements. In addition, the X-ray induced effects relative to absorbed radiation dose will be discussed. These values of X-ray dose are obtained using a recent development in the RADDOSE-3D utility[3] for radiation dose estimation in small molecular systems.[4] The changes observed in the behaviour of the different catalyst materials within this transition metal-chloride-complex family will be presented with respect to structure and chemical properties. This work thus presents an insight into the stability of these industrially significant materials and opens the path for promising future work in damage mitigation strategies, made important by the development of new generation X-ray sources. References [1] C. Blake and D. Philips, Symposium of the International Atomic Energy Agency, 1962, 183. [2] E. F. Garman, Acta Crystallogr., Sect. D, 2010, 66, 339-351 [3] C.S. Bury et al., Protein Sci., 2018, 27, 217-228 [4] J. Christensen et al., IUCrJ, 2019, 6, 703-713

P3.1

Thermodynamic properties of selected liquid lithium alloys

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Nowadays, many new ways of storing as well as transmitting electricity are heavily researched. Although there are already many battery systems, lithium batteries are currently finding more and more applications on the consumer market [1]. Thermodynamic properties, phase equilibria and phase transitions are data of crucial importance when developing electrodes for batteries. Tools used for this process are different types of thermodynamic bases, containing the necessary information. However not all systems have been tested experimentally, therefore thermodynamic databases need to be constantly updated. In this work we propose liquid alloys from Ga-In-Li and Ga-Ge-Li systems as electrode materials for liquid metal batteries. A schematic illustration of such device is presented in Fig.1. There is a lack of thermodynamic data in the literature on these two systems, which results in the need to conduct experimental studies of the above-mentioned systems in order to obtain the necessary



data.

The two selected ternary systems consist of 5 two-component systems: Ga-Li [3], Ga-In [4] In-Li [5], Ge-Li [6] Ge-Ga [7]. Electromotive and calorimetric tests were carried out in the selected systems.

This work presents thermodynamic information about the Ga-In-Li and Ga-Ge-Li phase diagram. Moreover electromotive force measurements were conducted for the mentioned systems.

The cells were prepared using a glovebox chamber with protective argon atmosphere. Eutectic KCI-LiCl and LiF-LiCl salts were used in the preparation of the electrolyte. The construction of the cell is shown in Fig 2.



Fig. 1. Cell schematic of liquid metal battery [1].

Fig. 2 Illustration of cell for EMF measurements.

The obtained results will be used to optimize the thermodynamic properties of the phases present in the ternary Ga-In-Li and Ga-Ge-Li system, and for calculation of the phase diagrams of binary and ternary systems.

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Influence of different types of catalysts on pyrolysis process

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Energy sector is a driving force for development of economic countries [1]. Nonetheless the main energy sources all over the world are fossil fuels like coal, nature gas and oil, which usage leads to the formation of for example NOx, SO2 and CO2. The global movement is focused on the reduction of emission greenhouse gases [2]. This brings us to the point where energy sector must use energy sources that are both ecological and economical. One of the options which meet these requirements is thermal conversion of biomass. The pyrolysis seems to be promising one, this process occurs in temperature range from 300 °C up to 700 °C in anaerobic environment. It is leading to production solid (biochar), liquid (biooil) and gaseous products with different efficiency depending on process parameters [3, 4]. This paper is focused on the catalytic pyrolysis. The main aim of the application of catalysts is to improve the quality of products compared to normal pyrolysis. Well-known catalysts such as Ni, Mg or Fe promote production of hydrogen via methane reformation [5], as well as parallel reforming of hydrocarbons contained in the material and CO2 capture [6]. The catalyst can be applied, thus: i). in situ catalytic pyrolysis (the catalyst and the biomass feedstock are mixed in the pyrolysis reactor and the action happens within the same reactor) and ii). ex situ catalytic pyrolysis (the catalysts are placed in a separate reactor for catalytic upgrading of pyrolysis vapours). The catalyst should be characterised by appropriate properties such as specific surface area, micropore area, pore size distribution, framework structure, crystalline phase and crystallite size, and availability. The most often studied basic catalysts in pyrolysis are based on CaO and MgO: Ni-Mg-Al-CaO, Ni-Mg-Al-Ca and Ni-CaO-C [7, 8]. They are dedicated for fast pyrolysis considering their excellent deacidification, resulting in a lower acidity and a higher heating value of bio-oil [9]. To upgrade bio-oil from pyrolysis, various types of zeolites (ZSM-5, Y zeolite, MCM- 41 zeolite, ?-zeolite, and novel zeolite) [10] and solid acid (SiO2, Al2O3, Al2O3-SiO2) [11] materials are also extensively investigated. Moreover, transition metal oxides (TiO, NiO, ZnO, ZrO2, CuO, CeO2 and MnO2) have been employed in supporting catalysts to prepare heterogeneous catalysts [12, 13]. Hydrocarbon-rich products and pure oil is preferable as the final product of the process. Thus, the multifunctional catalysts are required for enhancing bio-oil quality by promoting hydrogen transfer and depolymerisation.

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P3.3 Sustainable materials applied to flexible electronics using a laser induced modular platform

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In recent years with the evolution of modern society, new and emergent technologies, such as flexible and wearable electronics, have been improving the overall well-being and human quality of life [1]. The great challenge of many researchers around the world is to continue pushing technology barriers further, exploiting the full potential of new smart devices and improving the already developed[2]. Toward devices that can be introduced in the future, it is necessary to have advanced sensors with high efficiency, light-weight, flexibility, durability, low-power consumption, biocompatibility, conformable properties and reproductible large-area manufacturing processes [3].

The flexible electronics family has been increasingly growing integrating high performance sensors, capacitors, light-emitting diodes, RFID antennas and so on[1]. Furthermore, flexible electronics can offer a novel range of applications, such as biological and environmental monitoring, energy harvesting and storage, intelligent robotics, electronic paper, smart clothing, flexible displays, healthcare sensors, and much more [4].

Over the past decade, various materials have received tremendous attention, as carbon materials, including graphite, active carbon, carbon nanotubes or graphene have focused most of the interest [5]. These present unique and advantageous properties such as excellent conductivity, thermal and chemical stability, high strength and outstanding flexibility. Also, these could be easily functionalized, giving them great features to be integrated as sensors as well as storage devices for various smart wearable devices [6].

Graphene is the one that stands out from this family of carbon materials, a one-atom thick layer of graphite arranged in a honeycomb lattice [7, 8].

As mentioned, it is essential to select and develop proper materials to be mass-produced in a reproducible, eco- friendly, and inexpensive fabrication process [1]. Currently, the graphene fabrication and patterning processes are mostly based on screen-printing, stamp-imprinting, inkjet-printing, slow-flow assisted assembly, photolithography, chemical etching and vacuum coating technology. Those conventional techniques generally require additional steps to improve specific proprieties on substrates increasing fabrication complexity, are expensive and time consuming which highlights the need to find sustainable alternatives [7, 9].

An alternative has been explored and appears to be one of the most promising approach (Figure 1). By using a laser-direct writing with a CO2 infrared laser, a one-step fabrication process is possible to prepare laser-induced graphene (LIG) under air conditions [10].

With this method, laser is focused to heat a specific zone and converts (photothermally) sp3 hybridized carbon atoms, found in substrates, into sp2 hybridized carbon - the carbon allotrope found in graphene [1, 10]. Laser generates a confined temperature field at a desired position with high controllability to produce a three-dimensional material. LIG has a superhydrophobic structure and could be doped with metal oxide nanocrystals, functionalized with polymers, or developed into vertically-aligned graphene fibers [10, 11].

The peculiarity of the LIG lies in its versatility, manipulating endless promising carbon materials as well
enabling a cost breakthrough and a rapid production of conductive patterns that can be structured designed in robust, thin, and conformable devices. Finally, the challenge and future perspectives of this work is creating a next-generation of flexible electronics toward the development of sensors and supercapacitors using a single low-cost fabrication process, and posteriorly be applied in smart wearable systems [4, 12].



Figure 1. Some preliminary results. Polyimide substrate transformed and used as electrodes for electrochemical biosensors (example of the proposed technique).

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TEM study of two-dimensional polymers for organic electronics

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Organic flexible electronics have received considerable attention in sensing, displaying, diagnosing, memorizing [1], with the possibility of low cost, ultralight weight, mechanical bendability and versatile chemical design. Among current materials for device fabrication, novel two-dimensional polymers (2DPs) are most promising due to their intrinsic structural stretchability, tuneable electronic properties including bandgap and conductivity, and considerable carrier mobility [2]. However, the practical feasibility of introducing novel 2DPs into flexible devices requires the premise with deep understanding of how the mechanical deformation affects their microstructure and properties. Here, we demonstrate TEM results for several novel 2DPs (including 2D polyimine and 2D hexaaminobenzene-Cu (HAB-Cu) for transistor device, q2D polyaniline for sensor device because of their great abilities of large-area synthesis and high crystallinity). TEM and high-resolution TEM were performed to image the crystallinity and molecular structures. The maximum degree of crystallinity ensures satisfied long-range carrier transport properties. TEM images are shown in Fig.1, 2D polyimine and 2D HAB-Cu exhibit high distribution of crystals and clear lattices, which reveals great ability of crystalline with assistance of surfactant in the interface between air and water. The domains can grow up to 150 nm and 50 nm, respectively. Electron energy loss spectroscopy (EELS) was used to verify its possibility of characterizing the changes of chemical bonds in 2DPs. Since electron beam is not stable and may cause drift and value jumping during the recording process, it is of great importance to firstly figure out whether EELS data is reliable and accurate enough. Additionally, the zero-loss peak (ZLP) is undetectable when the core loss peak is requiring, therefore we assumed that dynamic carbon K- edge peak instead of ZLP as a reference peak to quantitatively determine the movement of peaks to eliminate the effect of drift would be meaningful. The EELS spectra of two kinds of 2D coordination polymers (CuNi(CN)₄ and CuPt(CN)₄) are shown in Fig.2. The core-edge loss intensities of two curves vary from each other due their different relative specimen thicknesses (t_R) under the same illumination step [3]. The EELS spectra show the carbon and nitrogen K-edge peaks of 2DPs and they deviate from standard peak values, which may be caused by drift. The peaks of energy loss can be assigned to $1s-\pi^*$ transition indicating the functional group of C=N [4]. The energy gap of relative difference between carbon and nitrogen peaks is identical to the gap between respective carbon and nitrogen peak of CuNi(CN)4 and CuPt(CN)4. This means values of different core-loss peaks change synchronously. After ensuring that there will be a same change between ZLP and carbon K-edge peaks could verify the feasibility of EELS. We are planning to use an in-situ push-to-pull manipulator in TEM as a tool to observe the mechanical behavior and failure process of 2DPs at molecular level.

P3.4



Fig.1. TEM image and SAED pattern of 2DPs. (a) 2D polyimine; (b) 2D HAB-Cu



Fig.2. TEM images with corresponding FFT patterns and EELS spectra of 2DPs. (a) CuNi(CN)₄; (b) CuPt(CN)₄; (c) Carbon K-edge peaks; (d) Nitrogen K-edge peaks

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P3.5 Synthesis of nano-sized metal organic framework using selectively modified clay nanotube for enhanced gas adsorption properties

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Metal organic frameworks (MOFs) are hybrid materials that consist of organic ligands and metal ions or clusters. Recently, increasing number of MOFs have been recognized for a great potential in CO2 capture due to their high surface area. Especially, HKUST-1 consisted of copper nodes and organic ligands is one of the most widely studied MOFs owing to its high porosity. In this work, we synthesized HKUST-1 in the lumen of modified Halloysite clay nanotubes (mHNTs). Here, HNT acted as a nanocarrier to load precursor solution of HKUST-1 inside and nano-size HKUST-1 was successfully synthesized in this limited cage. Furthermore, HNTs helped to protect HKUST-1 from water exposure. Experimentally, inner or outer surface of HNTs were selectively modified with sulfuric acid and (3-Aminopropyl)triethoxysilane. Each mHNT was designated EHNT and HNT-NH2. Then, HKUST-1 precursor was evenly loaded into the lumen of HNTs in a solution phase, and the crystalline MOFs were syntehsized via solvothermal method. The final procuct was named to EHNT@HKUST-1, HNT-NH2@HKUST-1 respectively. As nanocarriers, HNTs provided confining spaces to make specific boundary for growing MOFs with longitudinal axis of HNTs and improved water stability of MOFs. Also, selectively modified HNTs imparted unique properties to the surface of composites. Specifically, ething treatment through sulfuric acid provided effective method for expansion of lumen in HNTs and made it possible to maximize the loading of the precursor solution. Amine functionalization, meanwhile, granted more enhanced CO2 gas adsorption property compared to HNT@HKUST-1 composite. Gas adsorption capacity was analyzed by Brunauer-Emmett-Teller (BET) using N2 and CO2 gases. Specifically, EHNT@HKUST-1 composite showed enhanced CO2 gas adsorption capacity compared to HNT@HKSUT-1, being increased about 14.9 times, from 8.344 cm3(STP)g-1 to 19.332 cm3(STP)g-1. Additionally, HNT-NH2@HKUST-1 indicated around 24.849 cm3(STP)g-1 of CO2 gas adsorption capacity. These nanocomposites were analyzed by SEM, TEM-EDS and XRD in an effort to investigate the morphological and structural characteristics. This work can be a trigger to synthesize various hybrid nanotube materials for synergistic effects and applied to competitive adsorbents for gas capturing.

Slow disassembly of the germanosilicate UTL

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Zeolites are inorganic crystalline solids (mainly silicates or aluminosilicates) with three-dimensional microporous structures. The micropores provide zeolites with shape-selective properties. Therefore, the zeolites found various applications in separation and catalysis. Most notably, zeolites are used as heterogeneous catalysts in petrochemistry, oil refining and recently they have also been studied in fine chemical synthesis and biomass conversion.

Zeolites are commonly prepared by hydrothermal synthesis; however, discovery of new zeolites is often achieved by trial and error. On the contrary, the ADOR (assembly–disassembly–organisation–reassembly) process developed by Roth et al. [1] enables preparation of new zeolites whose structure can be easily set based on the synthesis conditions. The method exploits the lability within germanosilicate zeolites which contain Ge- rich double-four rings (D4R). The D4R units can be hydrolysed, leaving only the Si-rich layers. The layers can be subsequently reorganised and reconnected into a new structure. In summary, the method allows transforming one structure into another in a controlled and predictable manner.

UTL is the first 3D germanosilicate zeolite which was disassembled into layered IPC-1P material through selective removal of the bridging Ge-rich D4R units from the framework, while maintaining intra-layer integrity. Further manipulations with the IPC-1P under variable conditions produced several new zeolites (PCR, OKO, *PCS, IPC-7, IPC-9 and IPC-10) all comprising the same crystalline layers but differing in their connectivity. [2]



Figure 1. Subsequent transformation of the UTL zeolite to the IPC-1P, IPC-2P and IPC-2.

The hydrolysis of the UTL comprises of two simultaneous processes: the framework disassembly accompanied by Ge deintercalation, and spontaneous rearrangement of the framework (Figure 1). The disassembly proceeds rapidly (UTL is transformed to IPC-1P in less than 5 minutes) seemingly regardless of the pH or temperature. [3] On the other hand, the rearrangement (subsequent transformation of IPC-1P to IPC-2P) can be controlled by external conditions including the pH and temperature. For example, in low pH solutions the rearrangement is more favoured than in neutral solutions. [4]

Conditions affecting the rearrangement have been thoroughly studied; however, the disassembly has not yet been sufficiently described. Successful exploration of the disassembly requires slowing down its rate. Morris et al. [5] performed a study on hydrolysis of UTL using only small volume of water. While the low water content in the system succeeded in slowing down the disassembly rate, the low total volume of the solution prevented the zeolite from forming the layered precursor IPC-1P. Instead, the UTL directly transformed into the subsequent, thermodynamically more stable IPC-2P. Therefore it is arguable how similar are these conditions to the common ADOR protocol. Therefore, a system

P3.6

containing only small amount of water in a large volume of inert liquid would be more appropriate for investigation of the disassembly under conditions comparable to previous studies on the UTL germanosilicate. [3]

In this contribution we describe a method for slow and controlled disassembly of the germanosilicate UTL. We slowed down the rate disassembly by treating material with alcohol-based solutions. The alcohol does not attack the D4R units. It only dilutes the solution, and thus, slowing down the rate of disassembly. With the rate of disassembly slowed down, the $3D \rightarrow 2D$ transformation of the zeolite UTL can be studied in more detail and at the same time it opens up the opportunity for preparation of new materials.

First, we treated the UTL with water-alcohol solutions. The solutions succeeded in slowing down the hydrolysis; however, the leached germanium species were poorly soluble in the solution and deposited inside the channels. The deposition of germanium within the framework led to poor textural properties of the samples and questionable reproducibility of the results. Subsequently, we replaced the water-alcohol solutions with acid- alcohol ones (e.g. HCl in EtOH). The treatment with acid-alcohol solutions produced easily soluble germanium species, leading to materials with textural properties comparable to those described in literature.

When the UTL zeolite was treated with acid-alcohol solution it slowly transformed to the IPC-4 (PCR) zeolite over 60 days (Figure 2). However, when additional building blocks, such as Al3+, were added into the solution, the disassembly proceeded only half-way to IPC-2P, and then the material spontaneously transformed back to UTL. We address the importance of Al as additional source of building blocks involved in the restoration process of the structure transformation of UTL and simultaneously as a method for incorporation of catalytically active Al species.



Figure 2. Slow disassembly of the zeolite UTL monitored by the change of d-spacing between its layers.

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P3.7 Utilization of unique organic materials deposited by Atomic Layer Injection method

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Deposition allows to create thin films and layers on the functional materials that change the properties of bulk material. It opens a new opportunity for many applications in the research and industry. A variety of deposition methods were developed, including chemical and physical vapor deposition. They are based on material vapor which tends to impinge on the substrate. The thin layer is formed during exposition to volatile precursors in case of chemical deposition and in case of physical, the material vapor is gained from powder which is heated at high temperature and approaches to substrate. Nowadays it is possible to deposit thin film layers of different materials with accurate precision of nanometers, e.g. atomic layer deposition (ALD) and others. Whereas these methods are suitable for almost all inorganic and some organic materials, the problem occurs for the large organic molecules that need high temperature for evaporation from powder. At high temperatures the whole molecule can be eventually destroyed. Another problem is with bio-organics which cannot stand heating, like viruses, proteins, etc. There was some effort to deposit organics and bio-organics, but all methods had to face some problems. Typical example is electrospray deposition which uses liquid atomization by means of electrical forces generating a plume of droplets by charging the liquid at a high voltage [1]. Charged droplets are charging the insulating surface which can cause nuisance and the landing of the sprayed molecules is not soft which is destructive for them. There are few options to prevent these disadvantages by employing different methods, but they are really expensive, e. g. Electrospray Ion Beam Deposition method (ES-IBD) which consists of so called nano-electrospray, ion and electrostatic optics, quadrupole mass filter and time-of-flight [2]. However, these techniques can only be used with polar solvents, and typically deposition rates are very slow. One solution for deposition of these types of organics is a method called Atomic Layer Injection (further ALI) which is Pulsed Injection technique. Here, the injection of solution to the substrate in ultra-high vacuum chamber is performed. The injection is made by pulse valve which transforms solution to aerosol. The driving force for injection is given by argon gas which pushes the solution through pulse valve. The size of the drops of the aerosol can be controlled by adjusting the difference between pressure in the valve and pressure in the vacuum chamber. The solvent in droplets is evaporated during the flight, so only the molecules get on the substrate. The deposition by ALI method is suitable also for nanoparticles, nanotubes, pyrroles, polymers, bio-organics and other molecules. The main advantage consists of liquid phase of the solution with molecules which slows down the process of oxidation, e.g. ß-Carotene [3]. Other advantage is possibility to inject not just liquids but gases. The Atomic Layer Injection method allows to study properties of unconventional organic materials which have high potential in research and industrial field. It can achieve relatively high deposition rates. Furthermore, this technique is easy to use and cheap in compare to others. This technique in combination with annealing can provide deposing selfstructured layers. We present here initial results on deposition of single-molecule magnets (SMM) employing Atomic Layer Injection (ALI) technique. We tested [1,1'-Bis(diphenylphophino)ferrocene]dichlorcobalt(II) - DM18N and copper(II)dibenzoylmethane - Cu(dbm)2 molecules in powder. The molecular powder DM18N was dissolved in chloroform creating solution of concentration 3 mM. Second solution was prepared by mixing dimethylformamide solvent and Cu(dbm)2 molecular powder of concentration 1 mM. As substrates we chose Si(111) and Si(100) with Au layer coating because of its chemical stability. After deposition we observed real sample surfaces in Scanning electron microscopy to identify molecules in droplet formations. We also exploited Energy dispersive spectroscopy to confirm our presumptions. To assess their chemical composition, we used X-

ray photoelectron spectroscopy (XPS). We proved that molecules are appearing preferentially on the edges of droplets area and stay in form of nanocrystals. The solvent creates coffee-ring stains. Later on, we found out that coffee ring stains can be suppressed by heating the sample. Acknowledgments This work was supported by the Central European Institute of Technology Brno (CEITEC) under Grants MEYS NSP II, Project No. LQ1601 (CEITEC 2020), MEYS InterExcellence (No. TC17021) and H2020 FET Open PETER (No. 767227). References [1] Elzoghby, A. O. Implications of Protein- and Peptide-Based Nanoparticles as Potential Vehicles for Anticancer Drugs. in Advances in Protein Chemistry and Structural Biology vol. 98 169-221 (Elsevier, 2015). [2] RAUSCHENBACH, S. Electrospray Ion Beam Deposition. Rauschenbach Research [online]. http://rauschenbach.chem.ox.ac.uk/home#methods [3] Courtesy of F. Himpsel and C. Rogero (NanoPhysics Lab, Centro de Física de Materiales CSIC-UPV/EHU, San Sebastián, Spain).

P3.8 Synthesis of metal@molecular sieve composite catalysts with bimetallic nanoparticles for hydrogenation reactions

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Zeolites are highly porous crystalline solids (mostly aluminosilicates) that comprise tetrahedrallyconnected three dimensional frameworks and extra framework charge balancing cations. Their fascinating physical properties such as high sorption capacity, ion-exchange properties, shape selectivity and molecular sieving properties, catalytic activity allow to exploit them in various ways. Most widely these materials have found application as molecular sieves and heterogeneous catalysts in petrochemistry, oil refining and biomass conversion.

Despite the fact, that aluminosilicates have been well studied and are commercially used, isomorphous replacement of Si^{+4} in the zeolite framework by cations other than Al^{3+} such as Fe^{3+} for tuning of catalytic properties of the material remains a field of extensive studies [1-3].

It is worth noting, that a few recent studies have assessed the effect of iron on the catalytic properties of Pd catalysts in the selective hydrogenation of unsaturated compounds. [4] Undoubtedly, most selective hydrogenation catalysts are based on supported Pd, Pt, and Rh, which are usually dispersed in form of small (nano) particles [5]. However, production and recovery of these noble metals is very energy consuming and expensive procedure. Thus, at least partial replacement of these metals by other inexpensive metals without sacrificing activity and selectivity of the catalysts would be a major technological breakthrough reducing the ecological footprint, catalyst cost and potentially increasing catalyst stability [5]. Iron is a promising component for this role as it is a non-toxic, inexpensive transition metal, which is abundant in nature and also potentially amenable to magnetic recovery [6,7,8].

Another important factor, which can affect the activity of these hydrogenation catalysts based on noble metal nanoparticles is the choice of a matrix or a support. Most common ways of such catalyst preparation include either encapsulation of the active metal nanoparticles in a porous matrix [9] or dispersing them on a high-surface support. Zeolites among other supports (carbon, metal oxides and others) have the advantage of shape selectivity which can optimize the outcome of reaction by increasing selectivity to the desired product.

In this study we describe a proof of concept for preparation of bimetallic nanoparticles encapsulated into zeolite framework by reductive demetallation of Fe-zeolites. (Fig 1.)

First step, involves direct synthesis of Fe-silicates with MFI framework topology using modification of method described by Ratnasamy [10] by increasing Fe-content in the synthesis mixture up to Si/Fe ratio 25-30. This procedure is followed by calcination of samples to remove the organic template. Then structural and textural properties, framework topology are analyzed using XRD, SEM, low temperature N2 adsorption, UV-Vis.

In the next step, another metal is introduced into the synthesized zeolite via ion-exchange from the water solution. In this procedure the negative charge brought by the Fe³⁺ isomorphous incorporation in the zeolite framework is balanced by the second metal.

At last, ion-exchanged sample is reduced in the flow of hydrogen at high temperature. This step combines reductive demetallation of Fe particles and alloying them with the second introduced metal. Finally, the outcome material represents a siliceous framework of MFI topology with bimetallic clusters encapsulated into zeolite channels.



FeM@MFI

Figure 1. Overall scheme of the synthesis procedure for FeM@MFI, where M = Cu, Pt, Pd

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P3.9 Mechanical Reinforcement of Polymer Colloidal Crystals by Supercritical Fluids

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Colloidal crystals made of sub-micrometer polymer particles are volumetric and low-effort materials that are highly attractive for visible light photonics, GHz phononics and superhydrophobic coatings, to name a few. Nevertheless, their fragility is one of the main aspects limiting their application. We demonstrated a new concept for uniform mechanical reinforcement of colloidal crystals by means of supercritical nitrogen and argon, at temperatures well below the glass transition. This method, termed cold soldering, is a synergistic combination of nanoscale plasticization of particles? surface and compressive hydrostatic pressure. It results in the formation of permanent physical bonds between the particles while maintaining their shape and periodic arrangement. We employed Brillouin light scattering to monitor in-situ the mechanical vibrations of the crystal and thereby determine preferential pressure, temperature and time ranges for soldering This method offers a chemical-free and efficient solution for fabrication and tuning of durable devices and a potential remedy for the releasing of micro/nano contaminants into the environment. Moreover, the key idea of our approach, plasticization of polymeric nanostructures by means of gasses, remains an uncharted territory offering new effects and opportunities. Acknowledgements The work was supported by the Foundation for Polish Science (POIR.04.04.00-00-5D1B/18) and ERC AdG SmartPhon (Grant No. 694977).

P3.10 Mechanical and tribological characterization of (TiAl0.5CrNbY)Nx high entropy alloys: from micro- to nano-scale

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High-entropy alloys (HEA), consisting of at least five elements with almost equiatomic concentrations, have received large attention from the scientific and technological community due to their remarkable properties such as high hardness, high strength, good fatigue and corrosion resistance, and high thermal stability. These superior characteristics are due to HEAs specific nanostructure, consisting of nanoscale particles embedded in an amorphous and/or crystalline matrix. The aim of this study was to evaluate the mechanical and tribological properties of (TiAl0.5CrNbY)Nx protective coatings at micro- and nanoscale. The metallic and nitride films of TiAl0.5CrNbY high entropy alloy were deposited at 300 0C on OLC45 and Si(100) substrates by a hybrid high power impulse magnetron sputtering (HiPIMS)/direct current magnetron sputtering (DCMS)/radio frequency magnetron sputtering (RFMS) technique. A confocal unit, AJA ATC-ORION, was used, equipped with five unbalanced magnetrons fed by HiPIMS, DC and RF sources for simultaneous sputtering of elemental Al and Cr, Ti and Nb and Y targets, respectively, in inert Ar and reactive Ar N2 atmosphere. The hybrid deposition technique was used to improve the adhesion and to tailor the microstructure such as to obtain specific film properties. Films of (TiAl0.5CrNbY)Nx, where x= 0, 0.23, 0.42, with thicknesses in the range of 1-2 μ m, were prepared and investigated for chemical composition, morphology, structure and microstructure, adhesion and microand nano-tribological and mechanical properties by EDX/XPS, AFM, nanoindentation, nanoscratch, nanowear, XRD and SEM. All films presented an amorphous structure. The nano-scale hardness increased from 7.7 GPa to 33.2 GPa with nitrogen addition, while the nano-scale friction coefficient decreased from about 0.3 to about 0.1.

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P3.11 Structural and photoluminescent properties of porous silicon nanowires fabricated by metal-assisted chemical etching: influence of H₂O₂ concentration

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Samples of porous silicon nanowires were obtained by two step metal-assisted chemical etching (MACE) method using highly doped crystalline silicon wafers with a conductivity of <0.005 Ω^* cm. The hydrogen peroxide (H2O2) concentration used in the MACE was changed from 5 to 30%. Scanning electron microscopy showed that the resulting samples have double porosity, and the concentration of H2O2 affects the structural properties of the obtained samples. The diameter of the porous silicon nanowires varied from 50 to 200 nm, and the thickness of the double porosity layer from 400 to 900 nm, depending on the concentration of H2O2. Porous silicon nanowires were located on top, and a layer of porous silicon was located on the bottom. The concentration of H2O2 also affected the ratio of nanowire thicknesses to the porous silicon layer. Using the theory of the Bruggemann effective medium approximation, the porosity of the samples was calculated from the IR reflection spectrum, which was 40-50%. Electron microscopy demonstrated the presence of a large number of silicon nanocrystals in the volume of nanowires. These nanocrystals showed visible photoluminescence due to quantum confinement effect and had a core-shell structure: a SiO2 shell and a crystalline silicon core. The results presented in this work can be used to create optical sensors and porous luminescent theranostic nanoagents based on porous silicon nanowires for applications in sensorics and biomedicine.

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P3.13 Atomic resolution microscopy reveals the growth mechanism of 2D-CuO agglomerates synthesized via pulsed spark discharges in water

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Transmission Electron Microscopy (TEM) represents a powerful technique for material characterization, nowadays reaching atomic resolution in both imaging and elemental analysis. Beyond the use of TEM as a mere characterization tool, the information got by TEM is paramount for fundamental research, to understand the mechanisms of nanostructures interaction and self-assembly. This issue is also key to address nanomaterials synthesis and to tailor their properties. For example, while the employment of pulsed spark discharges in liquids has emerged as an easy method to synthesize a wide spectrum of nanomaterials, it remains difficult to be controlled.

In this work, we elucidate the growth mechanism leading to the selective synthesis of 2D mesoporous CuO agglomerates produced via pulsed spark discharges in water, thanks to the use of Atomic Resolution TEM. These nanostructures (sizes of 40-100 nm) are formed by the aggregation of small CuO nanocrystals (sizes between 3-5 nm). In our experiments, we exploited copper electrodes and water, and we selected four conditions by changing the voltage and pulse width. Atomic scale TEM analyses, in synergy with the electrical characterization of the discharge and the optical emission spectroscopy of the plasma radiation, led us to reconstruct the growth mechanism behind the 2D mesoporous CuO agglomerates self-assembly. We found that, although the material morphology and composition remain unchanged for all synthesis conditions, the crystal properties of the CuO nanoparticles can be finely tuned from mostly amorphous nanoparticles to high quality CuO nanocrystals. Moreover, while the CuO nanoparticles are almost spherical at lower pulse width, they become oblate at longer pulse width, reaching sizes of 6-8 nm in the elongated direction. Hence, at longer pulse width, the CuO nanoparticles are more densely packed in the 2D agglomerate.

We describe the growth mechanism of the CuO agglomerates as follows. Since Cu and O species are detected in the plasma, CuO nanoparticles form during the discharge. Their crystal growth is sustained by the plasma, during a time interval that is related to the plasma dynamics, leading to the formation of elongated nanoparticles at longer pulse width. The increased density of the agglomerates and the crystallographic characteristics of the CuO nanoparticles at longer pulse width may be also regarded as a consequence of the further crystal growth at longer plasma lifetimes. To explain the agglomeration of the CuO nanoparticles, we invoked the pressure gradients existing within the plasma, which encourage the aggregation of the nanoparticles in 2D-structures. This study opens the route for pulsed spark discharges in water as a mean to produce 2D mesoporous CuO agglomerates and confirms atomic scale TEM as a powerful approach to get insight in nanomaterials growth.

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P3.14 Pure Blue Fluorescent Organic Light Emitting Diode with an External Quantum Efficiency Near to the Theoretical Limit

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We present a pure blue fluorescent organic light emitting diode (OLED) where the emissive layer (EML) is composed of a host-guest matrix of 4,4'-di[N-carbazoly] diphenyl (CBP, host) and 4,4'-Bis[(N-carbazole) styryl] biphenyl (BSB4, guest). The optimized concentration of the guest in the host matrix yields a Commission Internationale de l'Eclairage (CIE) coordinate of (0.15, 0.13) which is very close to the National Television Standards Committee (NTSC) standard of blue color (0.14, 0.08). The concentration of guest is optimized at 6 wt% with the help of photoluminescence (PL) studies. We study the effect of the organic layers in the OLED stack to balance the electron and hole concentration in the EML, thereby improving the efficiency and its roll-off. The charge carrier mobility and molecular energy levels of the organic materials are taken into consideration for this optimization. The optimized device yields a maximum external quantum efficiency (EQE) of 4.08%. This is very close to the theoretical limit for EQE (5%) of fluorescent OLEDs without the use of any light extraction layer.

P3.15 High efficiency third generation oled using near infra red (NIR) material TPA-DCPP

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In this work we design and study high efficiency orange-red Organic Light Emitting Diodes (OLEDs) with the thermally activated delayed fluorescence (TADF) near infra red material TPA-DCPP as the emission layer. We demonstrate increased efficiency by employing guest?host system with TPA-DCPP as guest and a material with bipolar characteristics as host. A detailed study of the photoluminescence (PL) is performed by growing films at different doping percentages on glass substrates. The doping concentration is optimized to achieve the high luminescence efficiency and the desired CIE coordinate (colour purity). We design the OLED stack layout and optimize the stack for achieving maximum electroluminescence efficiency by attaining the charge carrier balance in the emissive layer.. A detailed analysis of the effect of injection layers on the charge balance and device efficiency is presented. From the study, a high efficiency orange-red OLED with a maximum EQE of 13.2%, a CIE co ordinate of (0.64, 0.38) and maximum current efficiency of 8.65 Cd/A is demonstrated.

P3.16 Electrophysical anisotropy of amorphous silicon surfaces nanocrystallized by femtosecond laser pulses

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High-power ultrafast (femtosecond) laser processing has been attracting scientific attention as a perspective tool for thin amorphous hydrogenated silicon (a-Si:H) films modification [1]. Such treatment increases electric conductivity and optical absorption of the films due to formation of Si nanocrystals and surface roughness, which is promising for photovoltaics. During such processing, laser-induced periodic surface structures (LIPSS) might also be formed owing to interference of incident light with excited surface plasmon-polaritons [2]. The a-Si:H films modified by ultrashort laser pulses demonstrate electric anisotropy [2], birefringence and dichroism [3], which can be used in thin-film optoelectronics, sensors and anti-reflecting coating designing [1].

In the present work 600 nm thick undoped and 300 nm thick phosphorous-doped a-Si:H films were irradiated by femtosecond laser pulses (1250 nm, 125 fs, 10 Hz) in a raster mode. The films were irradiated at various scanning speed resulting into 30 or 700 laser pulses acting at each spot of the processed area. Formation of various LIPSS with periods from 0.88 to 1.12 μ m and direction orthogonal or parallel to laser polarization was observed on the modified surfaces.

Raman spectroscopy with excitation at 633 nm revealed nanocrystallization of irradiated films. Calculated from Raman spectra the crystalline silicon phase volume fraction value varied from 17 to 30% within the modified a-Si:H films. The sizes of silicon nanocrystals are varied from 3 to 6 nm for undoped a-Si and were significantly less for phosphorous-doped film (1.6 nm). This size difference may be associated with a larger number of defects in the doped film, which prevent nanocrystals growth.

Due to laser-induced nanocrystallization the specific dark conductivity increases by 3 to 4 orders, up to $4 \cdot 10^{-5}$ S/cm for the undoped films, and up to 11 S/cm for phosphorous-doped a- Si:H. The LIPSS formation also induced anisotropy of dark conductivity in the modified a-Si:H film surface plane. The ratios of the latter differ up to 4 times in mutually orthogonal directions for each sample. Observed effect may be explained both by a LIPSS depolarizing effect and an uneven crystalline phase distribution. The photoconductivity of the undoped films also demonstrated anisotropy. Based on photoconductivity spectral dependences and absorption coefficient spectra analysis, this effect can be explained by the charge carrier lifetime anisotropy caused by uneven distribution of crystalline phase within a-Si:H films.

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P3.17 Tuning the magnetic anisotropy of SrFe< sub>12< /sub>O< sub>19< /sub> nanocrystallites

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Over the last few years, magnetic nanoparticles have gained increasing attention due to their potential use as building blocks for next-generation permanent magnets [1]. Among nanoparticles-based materials, ferrites with hexagonal structure such as SrFe< sub>12< /sub>O< sub>19< /sub> (SFO) play an important role in the quest for new technological applications [2]. In particular, the inherent anisotropic shape of the crystallites in such hexagonal ferrites makes them interesting candidates for hard/soft exchange-coupled magnets, thus, leading to the need of a systematic study of the magnetic interactions in such systems. The aim of this work is to demonstrate the efficiency and reproducibility of the sol-gel approach in the synthesis of SFO nanocrystals. We have investigated the effect of different thermal treatments to vary the size of the nanocrystals, obtaining almost isotropic nanocrystallites, with a platelet-like shape. Through X-ray powder diffraction (XRPD), transmission electron microscopy (TEM), and magnetic measurements, it seems clear that a significant relation exists between the morphology (i.e., size and shape), and resultant magnetic properties of the hexagonal ferrite, which show a clear dependence on the platelet size along the c-axis. In particular, the evaluation of the magnetic performance for permanent magnet applications shows similar values in all the samples, thereby demonstrating the feasibility of optimizing the annealing temperature without any worsening of the physical properties. Furthermore, we show that the intrinsic magnetic properties of the hexaferrite can be significantly improved by substituting Fe< sup>3+< /sup> with other suitable ions, such as Al< sup>3+< /sup> , which produces a remarkable increase in the coercive field, up to ~1T. Finally, we also discuss the use of SFO in bi-magnetic nanocomposites, by coupling it with a well-known soft magnet, CoFe< sub>2< /sub>0< sub>4< /sub>, through a simultaneous biphasic synthesis route developed previously [3,4]. By tuning the effect of confinement during the growth of both phases, we were able to control the size and distribution of the hard/soft-phase regions, as well as to tune the magnetic anisotropy by chemical engineering.

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Multiscale Simulation Framework for Functional Polymers

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For functional materials, the multiscale modeling of material structures and morphologies is of increasing importance [1]. The consideration of stimulus-induced property changes and the calculation of atomistic material parameters plays a key role [1,2]. Based on this idea, a methodology for the multi-scale description of the behavior of piezoresistive polymers is presented. The piezoresistive properties of the material are characterized by the coupling of the mechanical and electronic behavior in the material, which also depends on the macroscopic device geometry.

Specifically, we consider the application of such polymers as strain gauges on complex component surfaces [3,4]. Here, an isotropic strain determination in stress-increased surface areas shall be guaranteed. For this purpose we consider the bulk behavior as well as the interfacial behavior of the polymer. Exemplarily, we focus on Poly-3,4- ethylenedioxythiophene (PEDOT) based polymers.

Our multiscale approach consists of three steps. In the first step, molecular dynamics based load simulations are facilitated [4]. For this we use a standard force field [5] to calculate all elements of the elastic tensor. To determine the electrical resistance, the distances between pairs of molecules are considered in an *ab initio* method [6,7,8] which allows it to eventually compute the electron mobility as a function of strain. Finally, finite element simulations are employed to describe the behavior at the interface between the polymer film and the surface of the component.

Our methodology can be used to optimize existing piezoresistive polymers and predict the properties of new materials.



Figure 1. Schematic multi-scale workflow for the description of piezoresistive polymers.

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P3.18

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P3.19 Biodegradable porous silicon nanoparticles produced from silicon nanowires

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Aqueous suspensions of porous silicon nanoparticles (PSi NPs) were prepared by mechanical milling of porous silicon nanowires, which were obtained by metal-assisted chemical etching (MACE). PSi NPs are porous particles with a diameter of about 90 nm. Such PSi NPs were previously reported to be effectively used in imaging, diagnostics, and treatments [1-3]. Unique features of PSi NPs are their biocompatibility and biodegradability resulted in formation of nontoxic silicic acid as a product [4,5]. In present work, the dynamics of PSi NPs dissolution was studied in model liquid, i.e. sodium phosphate buffer (PBS) and in living cells, using optical methods. Raman spectroscopy showed that incubation of PSi NPs in PBS at 37°C leads to their complete dissolution. This was indicated by the Si-related band shift to lower frequencies, the decrease of Raman intensity and eventual complete disappearance of the band after 24 hours of incubation. It has also been proven by vanishing of PSi NPs photoluminescence incubated for 24 hours in 3T3 NIH living cells. The results are promising for development of high payload biodegradable drug delivery systems.

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P3.20 Diagnostic and radiotherapy improvement employing metallic biocompatible nanoparticles

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Significant improvements in diagnostic analyses of biological tissues and radiation therapy of diseased tissues may be obtained injecting in them biocompatible metallic nanoparticles at high adequate concentrations. In particular, Ag, Au and Bi nanoparticles, generally with spherical shape and diameter lower than 20 nm, prepared by laser ablation in water as pure or as functionalized molecules, can be inserted in biological tissues and organs to enhance their equivalent atomic number. The small dimension and the functionality of the bio-molecules for living cells allows to introduce the nanoparticles in the intracellular liquid through the cell membrane crossing, their diffusion toward the cell nucleus as well as their approach to the cellular DNA. This treatment, based on the increment of the local electron density, permits to improve the imaging diagnostics of the investigated tissues by using electron beams and X-rays, as well as the radiotherapy using X-rays, electron and ion beams. The high atomic number, in fact, enhances exponentially the X-ray absorption, the particle stopping power, the image contrast and the cellular DNA irreversible damage. The advantage to use biocompaticle nanoparticles were demonstrated using different physical techniques, such as Raman, UV-VIS, FTIR, XRD and EDX spectroscopies. The high Z of the nanoparticles in the solution shows effects of surface plasmon resonance, high mass absorption coefficient for photoelectric X-ray interaction, high electronic and nuclear stopping powers for electron and ion beams, as well as cell inactivation and damage at high absorbed dose. Preliminar mesurements in cell cultures and in living mice will be presented and discussed.

P3.21 Nanodiamond Magnetometry for localized free radicals detection in sperm cells

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Free radicals (FR) are short-lived reactive chemical species with one or more unbound electron. They are expected to be linked to various pathogenic conditions which impact male fertility. On the other hand FR are also needed to maintain crucial physiological functions in sperms including capacitation. Several methods for free radicals detection have been applied to sperm cells, especially reactive oxygen species. Most of them are fluorescent dyes which usually bleach over time, and are not sensitive enough for small fluctuations in FR that trigger capacitation. Nanodiamond magnetometry potentially offers a complementary solution. It allows to measure nanoscale magnetic resonance signals with unprecedented sensitivity using the fluorescent nanodiamond (FND) probes. This is possible due to presence of nitrogen-vacancy centers (NVs) in a crystalline structure of FNDs. Since free radicals have a free electron spin, they cause a magnetic noise which can be measured and read out as an optical signal.

In this study we have shown for the first time that fluorescent nanodiamonds can be used as probes for detection of free radicals in single sperm cells. We have used commercial 70 nm oxygen terminated FNDs as well as functionalized with human serum albumin or amino groups. Then highly motile boar sperms were selected and immobilized on dishes coated with fibronectin or hyaluronic acid. Cells were incubated in Human Tubal Fluid (HTF) in order to induce their capacitation or modified-HTF (HTF medium without bicarbonate, calcium salts and serum) to keep them in an uncapacitated state. Both variants were treated with various concentrations of FNDs. The biocompatibility of probe was evaluated using MTT, DCFDA and membrane integrity assay. It has been found that at low concentration (1 µg/ml) nanodiamonds do not have any adverse effect on spermatozoa. Confocal and scanning microscopy images have shown that FNDs preferentially attached to the head of sperm cells. Finally, based on the T1 relaxation measurements inspired by equivalent concept in MRI, preformed on our home-built microscope we were able to evaluate changes in the amount of free radicals, in a single spermatozoa, before and after capacitation. These proof- of-concept experiments show that nanodiamonds magnetometry is promising tool for future clinical studies of correlation between free radicals production and male infertility.

P3.24 Probing deep trap states in P3HT using electroabsorption spectroscopy

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The organic semiconductors have emerged as a promising candidate in the optoelectronic industry due to their economical fabrication method over a large area. Due to the amorphous nature and structural disorder of these materials, there are defects in the systems which affect the optical and electrical properties. Although the spectroscopic techniques such as capacitance-voltage measurement, impedance spectroscopy, deep level transient spectroscopy (DLTS) can be used to determine the density of defect states and their energies, probing the deep traps and mid-gap traps in these systems are difficult. Apart from the DLTS, the other techniques focus only on the study of the shallow traps in the system. Here, we use electroabsorption (EA) spectroscopy to study the deep trap states in the P3HT, a well-studied organic photovoltaic system. The variation of EA signal with the applied DC bias shows a non-linear behavior as the voltage is changed to forward bias from the reverse bias. This deviation from the ideal case increases with the applied forward bias. This suggests a non-uniform distribution of the electric field inside the device. We attribute this non-uniformity to the accumulated charges near the electrodes and the trapped carriers in bulk and the interface of the device. We investigate the energy of the trapped carriers from the temporal evolution of the EA signal. The large decay time suggests the presence of deep trap states (at 752 meV and 813 meV) in the P3HT. The density of the trap states is also estimated from the strength of the EA signal in the forward bias.

P3.25 A hybrid of reduced graphene oxide grafted amine-functionalized NiO/ZnO toward attenuation of electromagnetic waves

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The explosive wireless technology by utilizing electronic systems in civil and military applications unavoidably generate the pollution known as the electromagnetic interference, so lightweight materials with high absorbing efficiency in over broaden bandwidth are highly in demands. In this work, a hybrid composite absorber constructed from reduced graphene oxide (rGO) and amine-functionalized NiO/ZnO was prepared via in situ reaction, which consisted a pyrolysis and surface modification of a heterobimetallic Ni-Zn-based metal-organic framework. The rGO sheet were found to graft successfully on the surface of NiO/ZnO. The hybrid displayed an excellent microwave absorbing performance in polystyrene matrix. The optimal minimum reflection loss reached to -42.5 dB at 13.7 GHz at the coating thickness of only 2.15 mm with 4.5 GHz effective absorption frequency bandwidth, corresponding to a reflection loss less than -10 dB (90% absorption). The grafting of rGO not only resulted the hybrid composite in larger contact area, but also benefited synergistic effects with NiO/ZnO to endow electromagnetic waves absorbing performance. The absorbing mechanism was mainly contributed to the enrichment of interfacial polarization, dipole polarization, dielectric loss followed by multiple reflection and scattering.

P3.26 Electrochemical assessment of two metallo-porphyrins (Mn&Zn) for histamine detection - application in fresh meat evaluation

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The level of meat freshness can be evaluated by monitoring the quantity of histamine. By measuring the level of histamine in a food product, we can easily detect early onset of spoilage, thus reducing foodborne poisoning (by identifying contaminated products) and food waste (by recycling products that are edible). In this respect, carbon-based screen printed electrodes (C-SPE) have been functionalized with two different metallo-porphyrins (Mn and Zn) and their response to different concentrations of histamine was recorded via cyclic voltammetry. Real-world samples (commercially available meat samples) were also used for the extraction of histamine and tested in the same conditions as the standard concentration samples. The C-SPE modified with metallo-porphyrins showed increased selectivity towards histamine as well as a decrease in the oxidation potential due to an improved electron transfer between the molecular complex trichloroacetic acid-histamine and the metallo-porphyrins [1,2]. This interaction was modelled using HyperChem® software and the activation energy for each metallo-porphyrin was estimated. The limit of detection for histamine has been calculated as 0.7 ppm. Keywords: histamine detection, porphyrin functionalization, screen printed electrode, electrochemistry, meat freshness.

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Index

Agati Marta	P3-13	p.88
Alekseeva Ekaterina	P1-13	p.47
Babacic Visnja	P3-9	p.85
Barah Dhruvajyoti	P3-14	p.89
Cardoso Jose	P2-4	p.55
Chudzik Edyta	P2-3	p.53
Dinu Mihaela	P1-14	p.48
Dluhos Jiri	4.1	p.19
Drewienkiewicz Aleksandra	P1-2	p.24
Fernando Nathalie	P2-10	p.67
Gasiorowska Iwona	P1-6	p.32
Gola Kewin	P1-5	p.30
Inaganti Naga Sai Manoj	P3-15	p.90
Iordache Ana-Maria	P1-15, P3-26	p.49,p.99
Janus Karol	P1-3	p.26
Kalha Curran	P1-11	p.45
Kampmann Steffen	P3-18	p.93
Krajnak Tomas	P3-7	p.81
Kuliś-Kapuścińska Anna	P2-6	p.59
Kurbanova Anastasia	P3-8	p.83
Li Qiong	P1-10	p.43
Liao Zhongguan	P2-5	p.57
Łepicka Magdalena	P1-8	p.38
Maksutova Daria	P3-19	p.94
Maltoni Pierfrancesco	P3-17	p.92
Mania Izabela	P1-1	p.22
Moiseev Daniil	P3-11	p.87
Mosig Mathias	3.1	p.17
Mullick Priva	P1-12	p.46
Mzvk Aldona	P3-21	p.96
Neuman Jan	3.2	p.18
Palatinus Lukas	4.2	p.20
Pana Iulian	P3-10	p.86
Park Sooji	P3-5	p.77
Prochwicz Marcin	P2-2	p.52
Sahoo Subhamoy	P3-24	p.97
Sander Christoph	P1-7	p.36
Schneider Gerd	1.2	p.12
Sebastiani Marco	2.1	p.15
Shepa Ivan	P2-7	p.61
Shuleiko Dmitrii	P3-16	p.91
Sieradzka Małgorzata	P3-2	p.70
Silomon Jendrik	P2-9	p.64
Silvestre Sara	P3-3	p.72
Soldatov Alexander	1.1	p.11
Stec Jacub	P1-9	p.40
		-

Torrisi Alfio	P3-20	p.95
Trelka Anna	P1-4	p.28
Veselý Ondřej	P3-6	p.78
Vu Thi Quyen	P3-25	p.98
Wozniak Krzysztof	1.3	p.14
Zabrocki Miłosz	P3-1	p.68
Zglobicka Izabela	P2-8	p.63
Zhang Bowen	P3-4	p.75
Zięba Amelia	P2-1	p.50