HUNGARIAN ACADEMY OF SCIENCES
CENTRE FOR ENERGY RESEARCH

29-33 KONKOLY-THEGE MIKLÓS ÚT
1121 BUDAPEST, HUNGARY

PROGRESS REPORT
ON RESEARCH ACTIVITIES
IN 2018
DEAR READER,

Welcome to the 2018 yearbook published by the MTA Centre for Energy Research (MTA EK), summarizing the scientific results of its three institutions and highlights in 2018. This booklet provides a summary of the research personnel and equipment of departments and research groups working in the Centre.

The year 2018 was average in terms of awarded grants and new opportunities. The National Nuclear Research Programme was successfully terminated with a large amount of new research results. On the 26th of March a new test laboratory was inaugurated for space research in the framework of news conference at the campus of our Research Centre. The laboratory was built according to the European Cooperation for Space Standardization and will provide a comprehensive ground for testing space products such as electronics or other parts of space crafts.

In the field of renewable energies important discoveries were published in the prestigious Nature Chemistry journal on cheap catalysts (MoS$_2$) for hydrogen production and in the Nature Energy on bio-ethanol produced from cellulose with fully integrated process to the existing fuel refinery factories. In the field of nuclear energy, a compact training simulator was developed for nuclear reactors, using the in-house developed simulation engine software and touch screens. Beside this, a significantly modernized environment monitoring system was designed and built for the Paks Nuclear Power Plant to replace the old system.

The Budapest Neutron Centre (BNC) became a member of the League of advanced European Neutron Sources on the 12th of September. This organization will work on the promotion of the neutron based scientific research and the harmonized open science environment including the open data idea. The BNC researchers continue their work in various EU funded projects such as IPERION, E-RIHS, BrightnESS and CHANDA. The Centre is involved in the preparation of the European Spallation Source project aimed at constructing the new neutron source facility in Sweden. Member countries are invited to contribute on an in-kind basis, and the expenditures of the participating institutions in Hungary are compensated from the membership fee of the country.

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**ABBREVIATIONS**
MISSION STATEMENT OF MTA CENTRE FOR ENERGY RESEARCH

- Research and development in the field of nuclear science and technology for facilitating the adoption and the safe use of nuclear technology in Hungary.
- To participate in international research effort aiming at the establishing a new generation of nuclear power plants and closing the fuel cycle.
- Maintaining and improving competence in nuclear science and technology, especially in the field of nuclear safety, security, health physics, nuclear and isotope chemistry.
- To guarantee the safe operation of Budapest Research Reactor (BRR), and to ensure the open access of the research facilities around the reactor.
- Research activities to improve nuclear analytical and imaging methods and their applications for energy and materials science.
- To perform studies in the field of environmental physics related to energy generation, renewable energies, energy storage and their impact on public health, and on environmental safety.
- Research and development in the field of low carbon energy technologies and of energy saving in industrial technologies.
- Interdisciplinary research on complex functional materials and nanometer-scale structures, exploration of physical, chemical, and biological principles, their exploitation in integrated micro- and nanosystems, and in the development of characterization techniques.
- Dissemination of the results in international programs, education and industrial research and development.

SCIENTIFIC ADVISORY BOARD OF THE MTA CENTRE FOR ENERGY RESEARCH

The Board consists of five Hungarian and two foreign leading scientists. The last meeting of the board took place in Budapest, on the 11th of April 2018. The management of EK presents usually an overview of the R & D activities in the previous year as well as figures about financial data, analyses of human resources and the dissemination of the research results. The R&D plans for the coming year and for the near future are also presented.

The Board members usually comment the presentations and ask questions. The French member of the Board offered help in the nuclear waste management topic and supported the continuation of this research. The German member of the Board pointed out that Siemens and other big companies have their own research bases. He supported our good contacts with small and medium enterprises. He was very satisfied to learn about the development of Institute for Energy Security and Environmental Safety’s “artificial leaf” results and asked why we did not patent it. The general opinion of the board was that Hungarian researchers were not socialized in making patents. It was also commented that if we patent a discovery we should initiate a start-up as well. One of the Hungarian member of the Board mentioned that the integration of Institute of Technical Physics and Materials Science did not cause problems, which is very satisfactory result of the joining process. The Board acknowledged that the internal research cooperation increases and provides successful results, which positively effects the mood.

Members of the Board:
- Prof. Dr. László Keviczky (Chair), MTA Institute for Computer Techniques and Automation
- Dr. Hervé Bernard (Deputy Chair), Centre French Alternative Energies and Atomic Energy Commission (CEA)
- Dr. Maximilian Fleischer, Head of Department of Corporate Technology, Siemens AG
- Prof. Dr. Ádám Kiss, Eötvös Loránd University
- Dr. Zoltán Homonnay, Head of Laboratory of Nuclear Chemistry, Eötvös Loránd University
- Mr. István Hamvas, Director General, Paks Nuclear Power Plant
- Dr. József Rónaky, Scientific Advisor, Hungarian Atomic Energy Authority
ORGANIZATION STRUCTURE OF THE MTA CENTRE FOR ENERGY RESEARCH
QUALITY MANAGEMENT

In order to achieve the highest quality of research, development, design, condition monitoring and valuation, engineering, contracting and managing in design, production, implementation and inspection, the Research Centre’s quality management system has continuously been upgraded by the recommendations of ISO 9001 standard since 1994. Reviewing our QM system by integral audits and management reviews, evaluating improvement opportunities, maintaining project documentation, infrastructure, supporting communication, ensuring the competence of workers the management improves the Centre’s QM system. For the new organization structure, our Quality Policy has been renewed. Many new employees induced a need to upgrade our QM tuition practice. We organised the work and fire safety educations. Our QM system has been certified by Hungarian Standards Institution, IQNet, MVM Paks NPP and MVM Paks II NPP. The last one gives concrete certifications for special topics; up to now three of them were awarded, one of these documents is shown below.

Certifications by Hungarian Standards Institution, IQNet, and MVM Paks NPP and MVM Paks NPP II
BUDAPEST RESEARCH REACTOR

One of the most important strategic large scale research facilities in Hungary is the Budapest Research Reactor (BRR). It serves the needs of an extensive and diverse scientific community by supporting R&D opportunities, helping innovation and providing a strong foundation for training and education.

BRR is a VVR-type reactor that uses light water as moderator and cooling fluid. The power of the reactor is 10 MW provided by low enrichment uranium fuel, and its main purposes - as established during the feasibility/functionality study - are radioisotope production, production of thermal and cold neutron beams for research and applications in all areas, development of new functional materials and neutron activation analysis.

The core is designed to have about 10-11 reactor cycles per year, each having a time-span of 10 days. We are committed to long-term safety and responsible operations, taking care of the wastes from the spent fuel coming from the reactor. Besides the temporary spent fuel storage pool, we also operate a long-term spent fuel storage building for the physical and environmental separation between the reactor and the spent fuel storage.

The reactor hosts three kinds of activities: the research activities utilizing neutron beams, production of radioisotopes for industrial and research purposes, and providing national and international training. We are proud of our innovative flagship research topics, which are carried out by a network of neutron beam stations, including beam-lines of thermal neutrons, experiments on powder and residual stress diffractometry, radiography, biological irradiations and beam-lines of cold neutrons for experiments on small angle neutron scattering, reflectometry, prompt gamma activation analysis and nuclear data measurements. In accordance with recent worldwide trends, we are open to establishing new industrial relations and supporting innovation. The BRR’s experimental facilities are open for science based on excellence for researcher all over the world. We aim to increase our competence in special topics, to implement new technologies and develop new materials, to promote and exploit our R&D capacity at the national and regional/international level. During the past years the BRR hosted several international schools on various technical and research topics, special trainings in the field of reactor physics, reactor operation, nuclear measurement techniques, and safety and environmental issues.
The Budapest Research Reactor (BRR) is used by groups of different scientific communities from medical, environmental, material, archaeological, nuclear sciences and industry, as well as several Hungarian Universities. Neutron beams are uniquely suited to study the structure and dynamics of materials at the atomic level. The Budapest Neutron Centre (BNC) coordinates the scientific utilization of the research reactor. Some of main research topics currently are:

- neutron scattering, used to examine changes of sample properties under different conditions such as variations in vacuum or pressure, high and low temperature, magnetic field, modelling real-world conditions.
- using prompt and delayed neutron activation analysis, it is possible to measure the concentration of elements in ppm and ppb levels even for small samples. Atoms of a sample become radioactive by exposure to neutrons from the reactor. They decay of gamma-rays characteristic for each element that can be detected by suitable detectors.
- neutron activation is also used to produce different radioisotopes, widely used in industry and medicine. For example, Y-90 microspheres to treat liver cancer are produced by bombarding Y-89 with neutrons, which captures them.
- testing reactor materials; materials are subjected to intense neutron irradiation which causes radiation damage of their crystalline structure. For instance, some steels become brittle. Thus the so called high-entropy alloys resisting embrittlement are to be used in nuclear reactors.
- production of radioisotopes for different applications such as medicine, sterilization and industrial use.
- applied research using neutron beams to produce images. Dynamic neutron radiography of cooling system of refrigerator or visualization of fuel burn in engine system of a car, and tomography of different materials and items.

The BNC provides researchers with 15 neutron-specific instruments; 13 of them are installed directly on the horizontal beam ports of the reactor or to the thermal and cold neutron guides, while the other 2 are placed at the vertical irradiation channels. The instruments are supported by a variety of sample environments and data analysis and visualization capabilities.

The BNC provides access to the international neutron user community through a peer-review system. Local scientists assist researchers and industrial users to find the appropriate neutron techniques that meet their research needs. The various neutron scattering instruments in BNC cater to a large number of users from Europe and have grown in strength and stature over the years.

BNC is a member of the League of advanced European Neutron Sources and CERIC-ERIC, and partner in recent EU Framework Programme projects (NMI3-II, CHANDA, IPERION, SINE2020, ESS-BrightnESS, E-RIHES).

BNC is strongly committed to the training of future professionals inland and all over the world in co-operation with the International Atomic Energy Agency. We cooperate with Hungarian universities (Budapest University of Technology and Economics, Éötvös Loránd University (ELTE), Pannon University, …), BNC accommodates students for laboratory practice to study nuclear-based techniques. A specialized course was developed for geology students of ELTE to introduce nuclear analytical techniques into their education. BNC organizes the Central European Training School on Neutron Scattering annually, to train young scientists for neutron physics and to attract new users. The school provides insight into neutron scattering, element analysis and imaging techniques and their applications to study the structure and dynamics of condensed matter.

The Budapest Research Reactor is open to the public. Members of the local communities and high school and university students are invited to visit regularly and learn more about the amazing nuclear science possibilities available at BRR.
According to the law, during the use of nuclear energy not only the release of radioactive substances into the air and water, but also the radioactive contamination of the air and the water environment should be checked. The latter task is carried out in the territory of KFKI Campus by the MTA EK Environmental Protection Service (EPS).

In 2018, EPS performed its work on the basis of the renewed Environmental Policy, which accurately reflects the frequency and characteristics of the measurements in the whole 27.4 hectares of KFKI Campus. These studies include monitoring of airborne gamma radiation, atmospheric fallout, gamma spectrometric and total beta activity test of air aerosol particles. They continuously develop their sampling and instrumentation equipment in order to ensure the continuous high quality of their work.

Other tasks include determining the exposure of site workers due to site exposure. In addition to the official, obligatory test, the employees' external exposure to workplace radiation is controlled by their own thermoluminescent dosimeters (TLDs), while possible internal radiation exposure is controlled by so-called whole body examination. EPS constantly develops these measuring systems, and upgrade them so that they can perform the tests as accurately as possible. Thus, in 2018, the whole body detector and bed motion electronics were renovated and the measuring system was supplemented with an irradiation instrument to ensure the quality of TLD tests.

A detailed report of the work of the Service carried out in 2018 can be found on the MTA EK website.

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I. EU OR NKFIH SUPPORTED RESEARCH ACTIVITIES
HUNGARIAN NUCLEAR RESEARCH PROGRAM

Árpád Farkas

Objective

The Hungarian Nuclear Research Program (2014-2018) is a research and development project funded by the National Research, Development and Innovation Office (NKFIH, project identifier: VKSZ_14-1-2015-0021; homepage: vksz14.kfki.hu). The participants of the consortium project are: Centre for Energy Research, Hungarian Academy of Sciences (MTA EK, as coordinator), Budapest University of Technology and Economics (BME), Hungarian Academy of Sciences Institute for Nuclear Research (MTA Atomki), National Public Health Centre (NNK) and Nuclear Safety Research Institute Ltd (NUBIKI). The main objective of the project is to conduct high level research on the technologies supporting the long-term and safe use of atomic energy and to maintain and extend the Hungarian nuclear professional knowledge. One of the main efforts of the project is oriented towards providing the technical and scientific background for the safe operation of the existing reactor blocks of the Paks Nuclear Power Plant (NPP) and preparing for the installation of the new reactors. State-of-the-art research on the safe disposal of spent fuel and development of novel approaches to study different aspects of new generation reactors are also organic parts of the project. Elaboration of the mid-term strategic plans of the Hungarian nuclear research infrastructure is also in focus within this complex research program.

Results

In the last year of the project, significant progress was achieved in each of the three main task groups, namely: (i) experimental nuclear physics; (ii) simulation of reactor processes; and (iii) nuclear waste management and research on new generation nuclear power plants. Among the most important research results in the field of characterization of new reactor materials it is worth noting that the cladding of the first (15-15Ti) and second (SiC/SiC) ALLEGRO reactor zone is stable in a high temperature He atmosphere even in the presence of impurities. Both mixed oxide (MOX) and uranium dioxide (UOX) fuel types may be appropriate for use. The most important achievement in the field of structural integrity analysis was the development of an optical method able to track the geometrical evolution of the fuel samples during the experiments. In 2018 important code development has been carried out. All the elements of the VVER-1200 reactor code system have been developed and validated. A Multiphysics-type reactor analysis system was developed by linking the physical models with the fuel-behaviour algorithms. A complex Computational Fluid Dynamics (CFD) analysis has demonstrated that in the case of mixed fuel the thermal shield can provide appropriate protection of the MOX subassemblies even assuming a significantly lowered coolant flow rate. Another important result of the new code developments was the extension of FUROM-FBR fuel-behaviour analysis code to the case of sodium and lead cooled fast reactors. In the field of the sampling and analysis of beta- and gamma-active isotopes, new methods for the characterization of $^3$H, $^{14}$C, $^{36}$Cl, $^{79}$Se, $^{99}$Tc, $^{107}$Pd, $^{108m}$Ag and $^{129}$I nuclides dispersed in the fluid waste of Paks NPP have been developed. Important mechanisms of action of the low dose radiations at cellular level have been described. In addition, progress in identification and quantification of Deoxyribonucleic Acid (DNA) damages (deletions) has been made.

Remaining work

The project has finished in 2018.

Related publications


THE ALLEGRO PROJECT

János Gadó, Ákos Horváth, Zoltán Hözer, Gusztáv Mayer

Objective

Corresponding to the European initiative on launching research in the field of Generation IV nuclear reactors, the nuclear research institutes of the Visegrad 4 (V4G4) countries and the French CEA started a co-operation on the development of the Gas Cooled Fast Reactor demonstration reactor ALLEGRO in 2010. The final objective of the co-operation is to build up and operate this reactor but the construction has to be preceded by a long period of research and development related to various technological issues and the design of the reactor has to be prepared in several steps. ALLEGRO can start operation not earlier than in 2030.

Methods

The ALLEGRO Project Preparatory Phase was launched by the consortium of the V4G4 in 2015. In the preparatory phase of the ALLEGRO project (2015-2025), the conceptual design will be elaborated and the necessary research-development-qualification tasks will be executed. During the design of ALLEGRO the usual design methods will be applied. First, a pre-conceptual design shall be elaborated using the existing CEA 2009 Design with the necessary additions and modifications by a deadline of about 2020. Design additions and modifications are motivated by the safety concerns related to the CEA 2009 Design. After 2020 the conceptual design will be elaborated (by about 2025) which will be the basis of submitting the construction license application. Elaboration of the detailed design, construction, commissioning and operation will be a task of a new consortium.

Results

In the framework of the ALLEGRO project several basic documents have been created (ALLEGRO Design and Safety Roadmap, ALLEGRO Safety Requirements) and others are gradually actualized (ALLEGRO Design Specifications, ALLEGRO Research and Development Roadmap, ALLEGRO Business Plan, ALLEGRO V4G4 Concept Database). They show the directions of the design works. The Horizon 2020 project VINCO was finished in 2018. It significantly contributed to the ALLEGRO project by benchmarking reactor physical and thermo-hydraulic computational models. Several technical solutions concerning safety related issues have been analysed, like strengthening the guard vessel to reach a higher back-pressure hydrogen injection in loss of coolant accidents.

The Hungarian National Nuclear Research Program (NNKP) was completed in 2019. The program gave the possibility to prepare a lot of studies in line with the ALLEGRO Design and Safety Roadmap. New reports were issued by MTA EK [1-4] (most of them are described in details elsewhere in this Yearbook) and its Hungarian partners NUBIKI and BME NTI.

Remaining work

The finalization of safety relevant solutions requires further studies.

Related publications

Zirconium Materials Science Studies

Zoltán Hózer¹, Ildikó Szenthe¹, Márta Horváth¹, Ferenc Gillemot¹, Erzsébet Perez-Feró¹, Tamás Novotny¹, Zsolt Kerner¹, Nóra Vér¹, Márton Király¹, Richárd Nagy¹, Attila Nagy¹, Ádám Almási¹, Péter Szabó¹, Katalin Gmelinti¹, Timea Kocsis¹, Róbert Farkas¹, Levente Illés¹, Anna Pintér Csdóas¹, Katalin Balázi¹, Csaba Balázi¹, Zsolt Endre Horváth¹, Noémi Szász¹, Zsolt Fogarassy¹, Mária Dobosy¹, Dániel Antók¹, Levente Tatár¹, József Cselovszki¹, Valér Gottlasz¹, Gábor Baranyai¹, Martin Steinbrück², Ulrike Stegmaier², Péter Sipos³, Máté Szabó³

¹MTA EK, ²Karlsruhe Institute of Technology (KIT), ³MTA CSFK

Objective

In the second year of the project several experiments were performed in order to simulate those phenomena that can have an effect on the properties of Zr cladding in a nuclear reactor. The examination of the tested samples aimed at identification of microstructural changes. The main objective of the numerical modelling was the detailed analysis of cladding behaviour during mechanical tests.

Methods

The following experimental techniques and numerical methods were applied according to the detailed project plan in 2018:

- The irradiation of 186 Zr samples was continued in the Budapest Research Reactor for two more irradiation cycles.
- High pressure corrosion phenomena were investigated in autoclaves at 270 °C and 300 °C simulating the reactor core inlet and outlet conditions with five different coolant compositions. The treatments lasted up to 112 days. The mass gain of samples was determined on the basis of weight measurements.
- A new device (ELEMENTRAC® OH-p type analyser) was used to determine the absorbed hydrogen content in the Zr samples.
- Four-point bending tests, mandrel tests, axial and tangential tensile tests and ring compression tests were applied using a tensile test machine.
- Neutron activation analysis, profilometry, metallography, microhardness measurement, SEM, TEM and XRD techniques were applied for the examination of the as-received and pre-treated Zr samples.
- High temperature furnaces and thermogravimeter were used to investigate the behaviour of Zr samples during oxidation. The burst of cladding tubes was recorded by high speed camera (Fig. 1). Cladding creep due to high internal pressure at high temperature was investigated with pre-hydrided Zr tubes.

Figure 1: Cladding burst at high temperature recorded by high speed camera

- Finite element numerical models were applied for the simulation of mandrel tests with pre-hydrided samples. The effect of H content was taken into account in the modified Young modulus, which was specified as input data for the calculation.

Figure 2: Shape of experimental (left) and simulated (right) cladding specimen after mandrel test
Results

The fifth and sixth irradiation cycles were successfully completed in the Budapest Research Reactor. The total irradiation time of Zr samples exceeded 1700 hours.

Only modest mass increase was measured after autoclave treatments of Zr samples. The maximum mass gain was measured in case of high purity water, while the realistic coolant compositions were characterised by less corrosion.

On the basis of ring compression tests with pre-treated samples (electrolytic and high temperature charge of hydrogen, oxidation in steam and high temperature treatment in inert gas atmosphere) the ductile-to-brittle transition parameters were determined. The four-point bending tests characterised the load bearing capabilities of oxidised long cladding tubes with and without burst.

The steam oxidation of Zr samples resulted in the increase of ultimate tensile strength (UTS) at low degree of oxidation. Longer oxidation times resulted in brittle behaviour. The tensile tests indicated that the quenching of samples after high temperature treatment in inert gas atmosphere lead to the increase of UTS by 25%.

The main components of Zr alloys were determined using neutron activation analysis. The different Hf and Fe contents of E110 and E110G type alloys could well be distinguished.

Detailed geometrical data were collected using a laser profilometer on the deformed tubes of the CODEX-LOCA-200 experiment.

The structure and the layer thicknesses of the oxidised Zr samples was determined by optical microscopy. Nitrid grains were identified in samples which were oxidised in nitrogen reach steam or air.

The SEM investigations indicated that fragmented and layered oxide layers can be formed on the sponge based E110 alloy during high temperature (1000 ºC) oxidation in air (Fig. 3). The lamellar structure of Zr oxides formed at 1200 ºC during oxidation in steam were found with TEM technique (Fig. 4).

According to the Vickers type hardness measurements the treatment at 800 ºC did not result in the change of microhardness compared to the original state. However, the treatment at 1200 ºC increased the microhardness by 25%.

The results of the high temperature oxidation measurements both in steam and air proved that the traditional E110 cladding material is more susceptible to the breakaway oxidation than the sponge-based E110G alloy. The flow rate of the oxidising medium and the temperature overshooting at the beginning of the tests have significant impact on the oxidation kinetics of the zirconium alloys.

The oxidation of pre-hydrided Zr samples in high temperature steam (Fig. 5) showed that oxidation kinetics was not influenced by the hydrogen content of the samples.
Figure 5: View of electrolitically pre-hydrided E110 samples after oxidation in steam at 1200 S for 690 s

Remaining work

Further measurements, examinations and calculations will be carried out according to the Zirconium Materials Science Studies project plan.

Related publications

SEVERE ACCIDENT EXPERIMENTS WITH NITROGEN INJECTION

Imre Nagy, Nóra Vér, Róbert Farkas, Márta Horváth, Zoltán Hózer, Péter Szabó, Gergely Szabó

Objective

The presence of nitrogen in the atmosphere during a severe reactor accident can influence the core degradation process. The main objective of the present work was the demonstration of the effect of nitrogen on the zirconium cladding oxidation phenomena at high temperatures in two different scenarios.

Methods

The integral experiments were carried out in the CODEX facility with electrically heated fuel rods. The cladding materials were Russian E110 alloys produced by different technologies. ZrO$_2$ pellets with 7.65 mm diameter were used inside of the rods and two tungsten heaters were applied. The rods in the bundle were fixed by three spacer grids made of Zr1%Nb alloy. The bundle was placed into a hexagonal shroud. The shroud material was Zr2.5%Nb alloy. The inlet junction was located at 20 mm and the outlet junction at 1020 mm elevation. The upper head of the test section was cooled by a water loop. The bundle was heated by DC power supply units.

Results

Two experiments were successfully performed.

The CODEX-AIT-3 experiment simulated a bottom-head failure scenario with penetration of air into the reactor core. The duration of air ingress phase was 1 hour and the maximum cladding temperature was slightly above 1600 °C. The analysis of the outlet gas composition showed that during the air ingress phase steam and oxygen starvation conditions were established. The partial consumption of nitrogen indicated the formation of nitrides. The temperature profile significantly changed during the air ingress phase: the maximum temperature moved from the upper section to the middle of bundle due to the intense chemical interactions in the less oxidized central part. The post-test examination showed that the rods were covered by significant amount of nitrides (Figure 1). This structure indicated that oxygen starvation took place in the last phase of the test. The presence of nitrides on the oxide-α layer interface shows that the Zr cladding was strongly concerned by air oxidation before oxygen starvation took place.

In the CODEX-NITRO experiment a loss of coolant accident was simulated with injection of nitrogen from hydroaccumulators. The maximum temperature exceeded 1700 °C and the bundle suffered severe degradation. The presence of nitrogen accelerated the steam-zirconium chemical reaction. Due to the low steam flowrate steam starvation took place and it resulted in intense steam-nitrogen reaction.

Remaining work

Post-test examination of the bundles will be completed.

Related publications


NORMAL OPERATION CALCULATIONS TO VALIDATE THE CREEP MODEL OF THE CODE FUROM

Katalin Kulacsy

Objective

Cladding creep plays an important role in nuclear fuel behaviour, as, together with fuel densification and swelling, it determines the size of the pellet-cladding gap while the gap is open, and relieves cladding stresses when the gap is closed. Creep depends on many factors, the most important ones being stress, temperature and fast neutron flux both instantaneously and integrated over time.

In order to validate a fuel behaviour code, the creep model has to be assessed, preferably using separate effect tests. The creep model of the code FUROM-2.1.1 has been validated against data from several experiments, both integral and separate effect ones. The present work extended this validation using creep data measured on pressurised samples irradiated in the Russian research reactor BOR-60 at different pressures, temperatures and fast neutron fluxes. The samples were over-pressurised, therefore the cladding creeped outwards. This situation arises in commercial reactors when the rod internal pressure exceeds the system pressure or when the pellet-cladding gap is closed and the rating increases, in the latter case the expanding pellet exerts the pressure on the cladding.

The work was supported by the National Research, Development and Innovation Fund of Hungary (contract number: NVKP_16-1-2016-0014).

Methods

The samples were 16 and 65 cm long sections of fuel cladding pressurised and sealed, irradiated in different locations in the reactor for different time periods. The test matrix consisted of a systematic combination of several pressure (hoop stress), fast neutron flux, temperature and irradiation time values. The radius of the samples was measured after irradiation.

During irradiation the cladding undergoes thermal expansion, elastic deformation, irradiation growth and creep. All these phenomena were taken into account in the simulations, together with the deformations caused by them. The thickness of the cladding is of special interest, since true stress is approximately inversely proportional to it, so its decrease due to outward creep has a positive feed-back effect.

Results

The calculation results showed that the creep model implemented in the code FUROM-2.1.1 yields too large deformations. For certain samples some data (irradiation temperature or final hoop strain) were not given as a single value but as an interval. In these cases, we could use the lowest temperature for the simulation and the largest measured hoop strain, but even with these settings the calculated creep was too fast (Fig. 1). The red dots correspond to samples where so much creep was calculated that the cladding thickness decreased significantly and due to positive feed-back the cladding ruptured which did not occur in any of the experiments. However, all tendencies (dependence of creep on time, stress, flux and temperature) were reproduced well by the simulations.

![Figure 1: Hoop strains calculated at the lower limit of the given temperature ranges vs. maxima of the measured hoop strain ranges](image)

The implementation of a new creep model into the code FUROM is under consideration.

Remaining work

The work has been finished.

Related publication

INVESTIGATION OF THE AXIAL PROFILE OF HYDROGEN-TO-ZIRCONIUM MASS AND ATOMIC RATIOS BY NEUTRON-BASED METHODS IN Zr FUEL CLADDING TUBES

Zoltán Kis, Boglárka Maróti, László Szentmiklósi

Objective
To determine the H-to-Zr ratio along the longitudinal axis of fuel cladding tubes following high temperature burst and oxidation of the currently used (E110) and the newly developed (E110G) types of Zr cladding tubes designed for NPPs.

Methods
Prompt gamma-ray neutron activation analysis and neutron imaging are well applicable techniques, as they detect hydrogen in zirconium matrix effectively. They offer direct and specific determination of the hydrogen content. The position-sensitive prompt gamma-ray neutron activation imaging (PGAI) driven by neutron radiography (NR) has been applied to fulfil this task. Localizing the irradiated volume to a smaller part of the sample yields spatially resolved compositional information. The localization could be carried out by positioning the sample in the collimated neutron beam with the help of a motorized sample stage and imaging. Two times seven tubes (from CODEX-LOCA-200 and CODEX-LOCA-E4 experiments, respectively) were measured at the NIPS-NORMA facility. Altogether around 29 gamma spectra were taken for each cladding tube with 5 mm increments. The obtained elemental composition data characterize the bulk composition of the irradiated volumes. The evaluation is based on the precise determination of pairs of prompt-gamma peaks originating from the two elements. The characteristic peaks used for the calculation were at 2223 keV and at 935 keV for H and Zr, respectively.

Results
The axial profiles of the H/Zr mass/atomic ratios obtained can be categorized into three groups in both LOCA experiments (Fig. 1.a). In LOCA-200 (Fig. 1.b) in the first group, there are cladding tubes (E110G: No. 1, 3, 5 and E110: No. 6) with no visible deformation, and the values fluctuate around 80 – 100 ppm showing no clear peaks. In the second group, the cladding tubes (No. 2, 4) have a visible burst, and the values show a clear peak (1200 – 1600 ppm) around the opening. The H-profile, however, does not show the usual two-peaks shape. In the third group, the cladding tube (No. 7) has a visible burst with two smaller openings, and the values show three smaller clear peaks (100 – 250 ppm), a pattern not seen before. In LOCA-E4 (Fig. 1.c) in the first group, there are cladding tubes (E110G, No. 1, 3 and 5) with visible deformation and a smaller opening after the burst; and the highest values fluctuate around 400 – 500 ppm showing clear peaks. In the second group, the cladding tubes (E110, No. 2, 4 and 6) have a large visible burst and fracture, and the values show the highest concentration of hydrogen (6000 – 7000 ppm) in a wide section around the opening. The H-profile, however, shows the two-peaks shape only for tube No.4, while for tubes No.2 and No.6 rather smooth profiles were measured. In the third group, where the maximum burst pressure was applied, the cladding tube (E110G, No. 7) has a visible burst with one larger opening, and the values show a smaller clear peak (1600 – 1800 ppm) at it. This categorization could help to better understand the processes if the experimental history of these tubes would be related to the hydrogen profiles.

Figure 1: (a) The geometrical arrangement of the cladding tubes in the CODEX-LOCA-200 and –E4 experiments. (b) and (c) The longitudinal profiles of the H/Zr mass ratios (blue line) and the atomic ratios (red line) in CODEX-LOCA-200 (b) and –E4 (c) experiments, respectively. The red labels mark the tubes whose hydrogen profile have clear peak(s).

Remaining work
The project was finished as planned.

Related publication
IRRADIATION OF FUNCTIONAL MATERIALS

Ilidió Szenthe, Ferenc Gillemot

Objective

Functional materials are the common name of the safety related, but not structural, materials built into the primary system of the future fusion devices. Typical functional materials are the optical elements, cables etc. The EUROfusion WP-MAT program has a subproject to test the ageing under irradiation of the functional materials. Optical elements (e.g. lenses) are planned to be used in the instrumentation system of the future DEMO reactor. Gamma and neutron irradiation may cause degradation of the optical properties. The decrease of the wave transmission factor is the main interest. The task is shared between the Spanish CIEMAT (Centre for Energy, Environment and Technology, Madrid) and the MTA EK.

Methods

CIEMAT selected and provided 65 samples: different silica grades, spinels, yttrium-aluminium-garnet (YAG), sapphire, diamond, alumina, BaF_2, CaF_2, ZnS and coated versions of these types of materials. The task of MTA EK was to irradiate these samples in the Budapest Research Reactor. The irradiation requirements were 0.1 dpa, 0.2 dpa, 0.4 dpa, and 1 dpa fast neutron fluences, calculated with the cross section data of the Eurofer steel. The requested irradiation temperature was 250±10 °C. Two irradiations were performed in 2017 and 2018 in the BAGIRA temperature controlled irradiation rig. The irradiation rig can accommodate 6 different target holders. The target holders are 21*25*65 mm size aluminium blocks. Holes are drilled in the target holders for the specimens (see figure 1). During irradiation the target holders are heated by the radiation and temperature controlled by the flow rate of helium-nitrogen gas mixture inside the rig. The helium is a 10x better heat conductor than the nitrogen. The temperature of every target holder is measured by thermocouples, and auxiliary electrical heating is used to eliminate the temperature differences among them. Every target holder includes a set of dosimetry foils to measure the actual fluence. The irradiation time to reach the required 1 dpa fluence was estimated to be 2400 hours.

The design of the target holders was a very difficult task due to the unusually large number of very thin and fragile specimens. A further difficulty was to manipulate the irradiated (radioactive) samples. A few of them remained below the allowed activity level, but some others became highly radioactive.

Results

In 2017 and 2018 the irradiations up 0.4 dpa were finished, and the target holders were withdrawn from the reactor and opened. Since some samples became too radioactive, the 1 dpa irradiation was interrupted and after a sample selection it was continued.

The samples irradiated up to 0.4 dpa have been prepared for transport to CIEMAT. The treatment of the samples required a lot of development to be able to manipulate the very fragile radioactive materials.

Remaining work

As was mentioned above the completion of the 1 dpa irradiation has been delayed, and will be finished in April, 2019. In 2019 two transports will be organized to carry the samples to CIEMAT. The optical testing of the irradiated samples will be the task of 2019-2020. Also, in 2019 the dosimetry foils will be evaluated and the final irradiation report should be prepared.
**Objective**

DEMO will be the first fusion reactor producing electricity. The design of it has been started. In support of the design work there is a research and development project, “EDDI WP-MAT”, initiated by the EUROfusion Project. One part of the project develops the rules for determining the dimensions of the structural elements, and the other part collects the available data for the materials that will be used in DEMO. Among such materials are the low activity ferrite-martensitic steel of Eurofer, and the functional materials. The functional materials are the dielectric (e.g. cable insulation) materials and the optical materials. Optical materials are the lenses and windows planned for use in DEMO instrumentation and in the heating system. These windows are used to transfer all types of electromagnetic waves (e.g. light, infrared, microwaves etc.). The data provided by research laboratories are first typed into the database, then evaluated and the relevant ones are included into the Material Properties Handbook (MPH). The task of our institute is to plan and elaborate the structure of the databases and the MPH, collect the data, and finally prepare and edit the MPH.

**Methods**

The first step is to determine the database structure. In some cases, there are ready or semi ready databases (e.g. for Eurofer). In other cases, the database structure should be extended. Several types of data will be collected: production information, mechanical properties (e.g. yield strength, fracture toughness etc.), physical properties (heat conduction, density, etc.), chemical composition, optical properties, dielectric properties etc. Where the material ageing is important, the aged properties determine the lifetime of the structure. Generally, 25-30 properties are considered, depending on the material type and its use (e.g. optical properties are not relevant for structural steels, and the elongation is not considered as a property in case of optical elements). The collected data are evaluated and included into the MPH. First the data base structure (the relevant properties) is determined and after that average and lower bound curves are elaborated for the designers. The properties are separately provided for the as-received-new and service-aged materials. Typical aging damages are the radiation effects, thermal ageing, fatigue, creep etc. In some safety related cases, the data are given in both figures and tables (e.g. Eurofer), in other cases only diagrams are used. Figure 1 shows some examples from the Eurofer and the functional materials handbooks.

**Results**

Presently, the most recent version of the Eurofer MPH is finished and the structure of the Functional Materials MPH is set and available. A large amount of data is already available in the Functional Materials MPH.

**Remaining work**

The preparation of the databases and MPH-s is a continuing work. Some new data are already available for the existing volumes, and new volumes are planned (tungsten alloys, CuCrZr alloy).

**Related publication**

ADVANCES IN THE ATLAS+ PROJECT

Levente Tatár

Objective
An important part of the MTA EK participation in the ATLAS+ (Advanced Structural Integrity Assessment Tools for Safe Long Term Operation) project is a “medium” range experiment consisting of experimental study of crack propagation in an 1:5 mockup (MU) of the VVER-440 main feedwater nozzle [1]. This experiment, along with suitable FEM (Finite Element Method) models will increase the validity of the simulations. The experiment will be carried out in close cooperation with BZN (Bay Zoltán Nonprofit Ltd. for Applied Research).

Methods
The basic concept briefly: An extension arm will be welded to the VVER-440 mockup. A notch will be manufactured in the MU by EDM (Electrical Discharge Machining) followed by fatigue precracking. The final experiment aims at crack propagation by applying force to the extension arm. During experiment forces and displacements will be measured.

In the preparatory phase several problems have been identified, leading to important changes of the experimental setup. Most important changes are:

− The originally considered pipe-type arm can’t carry enough bending moment, so a solid arm will be used.
− Pulling instead of pushing is more advantageous, thus the former will be used.
− It has been revealed that due to the fact that large deflections may occur during the experiments, large lateral forces will develop. The testing machine is not designed to withstand large lateral forces, therefore they have to be limited.

To handle this problem, many different constructive solutions have been designed. After preselection two candidate solutions remained: MTA EK solution with guiding pins and BZN solution with oriented pulling bar. (See Figure 1.) Finally, BZN solution has been adopted.
− As there is a large uncertainty regarding material properties at the location of crack front it has been decided that a part from the original MU will be cut by EDM and will be used for additional material testing (see cutaway on Figure 1, b).

Results
Both analytical and finite element solutions have been used to design the experiment. A large amount of work has been done for designing the supporting structure. Weak points of the structure have been identified, modifications have been considered.

However, there are large uncertainties regarding maximum force and maximum deflection so the design has to be based on a “worst case” scenario.

Remaining work
Due to the large uncertainties besides the main MU from the STYLE (EU FP7) project two other MUs will be tested, too. Thus the test setup can be checked before performing tests on real reactor steel. The workpieces from which these MUs will be manufactured have been machined, they will be welded with the same electrodes and process as the original STYLE MU.

As these experiments are in preparatory phase, the main results of the experiments are still ahead.

Related publication
NONDESTRUCTIVE EVALUATION (NDE) SYSTEM FOR THE INSPECTION OF OPERATION-INDUCED MATERIAL DEGRADATION IN NUCLEAR POWER PLANTS — NOMAD

Ildikó Szenthe, Ferenc Gillemot, Antal Gasparics, Gábor Vértesy

Objective

NOMAD EU project focuses on the non-destructive investigations of RPV (Reactor Pressure Vessel) steels to better assess their integrity for lifetime management. The primary goals of NOMAD are:

− development and calibration of an NDE (Non Destructive Evaluation) tool for the in-situ inspection of cladded RPV material, which can have microstructure heterogeneities,
− validation of the surveillance programs with respect to the actual vessel under LTO (Long Term Operation) conditions.

In order to reach these goals, multiple NDE methods will be applied to multiple scales of samples in neutron irradiated condition: micromagnetic, electrical, ultrasound and acoustic emission methods. The results will be compared and combined in order to define a hybrid approach and finally demonstrate it in a modular way.

Methods

Within MTA EK a specially designed tool with a sensing yoke is applied for measurement of families of minor loops of the magnetic circuit differential permeability (MAT = Magnetic Adaptive Testing). The magnetizing coil is fed by a triangular waveform current with step-wise increasing amplitudes and with a fixed slope magnitude in all the triangles. The voltage signal in the pick-up coil is proportional to the differential permeability of the magnetic circuit. During the evaluation large sets of so-called magnetic descriptors from the measured data are delivered. The optimal descriptor as an output is selected by careful correlation analysis.

Results

A lot of experimental results were performed on Charpy impact tester and on block type specimens which were aged by thermal treatments. The team evaluated the results of the heat treatment study for A508Cl.2 and 15kH2NMFA reactor steel materials to ensure benchmark for the future measurements. The influence of heat treatment was unambiguously demonstrated by this method.

Influence of neutron irradiation was also studied. An example obtained on Charpy specimens made of 22NiMoCr37 material can be seen in Figure 1.

Remaining work

During the future measurements the hysteresis loops of the differently degraded samples will be compared and evaluation of loops will result in a large number of parameters, some of them characterizing the material degradation. This gives us a good chance, the measurement and evaluation will provide reliable data about material degradation.
CORTEX – CORE MONITORING TECHNIQUES AND
EXPERIMENTAL VALIDATION AND DEMONSTRATION

Sándor Kiss and Sándor Lipcsei

Objective
The CORTEX project is a four-year long, wide contribution between 19 institutes, universities and companies of 11 countries in several working packages. The consortium was strategically structured around the required core expertise from all the necessary actors of the nuclear industry, both within Europe and outside. The project aims at developing an innovative core monitoring technique that allows detecting anomalies in nuclear reactors, such as excessive vibrations of core internals, flow blockage, coolant inlet perturbations, etc. The technique will be based on primarily using the inherent fluctuations in neutron flux recorded by in-core and ex-core instrumentation, from which the anomalies will be differentiated depending on their type, location and characteristics. The method is non-intrusive and does not require any external perturbation of the system. The project will result in a deepened understanding of the physical processes involved. This will allow utilities to detect operational problems at a very early stage and to take proper actions before such problems have any adverse effect on plant safety and reliability.

Methods
We are participating in Working Package 4 (Application and demonstration of the developed modelling tools and signal processing) focusing on VVER-440 techniques against plant data measured at Paks NPP.

Results
For the project purposes longer and more frequent measurements were made than the regular ones at all four VVER-440/213 units of Paks NPP. Moreover, these measurements were virtually continuous for a whole fuel cycle at Unit 2 in order to choose periods as still as possible for the steady state measurements: one from the beginning, one from the middle and one from the end of the fuel cycle. The reactor instrumentation, relevant properties of the primary loop, the measurement system as well as the measurements and the reactor parameters are extensively described in deliverable D4.3 (Document describing all validation data), while the measurements are made available in the project repository. Additionally, we have coordinated the gathering of the contributions from the work package partners for deliverable D4.3 and edited it.

VVER-440 core data were assembled and provided for deliverable D4.2 (Core data for steady state calculations), additionally core loading data were also made available for the dates of the chosen noise data measurements. Since cross section data were not available due to legal restrictions, we will execute the core calculation code provided by the Technical University of Valencia.

Remaining work
The project finishes in 2021.

Acknowledgement
The research leading to these results has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 754316.
STRENGTHENING NUCLEAR SECURITY BY PARTICIPATING IN HORIZON-2020 PROJECTS

András Kovács, Péter Völgyesi

Objective

In order to strengthen nuclear security in Hungary and worldwide, the Nuclear Security Department of MTA EK got involved in three different Horizon-2020 EU projects. The aim of the C-BORD („effective Container inspection at BORDer control points”) project (2015-2018) was to develop, improve and test new comprehensive and cost-effective detection methods for higher efficiency Non-Intrusive Inspection (NII) of freight containers to be applied both at sea ports and at land border crossing points to disclose the illegal trade of e.g. cigarette, drugs, arms and radioactive and nuclear materials. Five different detection methods have been developed and tested at two sea ports (Rotterdam and Gdansk) and at a land border crossing place (BCP) at the Hungarian-Serbian border in Röszke.

The objective of the INSIDER project (2017-2021) is to improve decommissioning and dismantling (D&D) of nuclear facilities with medium and high radioactivity levels and/or other constrained environments from complex non-standard facilities, with regard to waste production. Thus, the project aims at improving the management of waste from nuclear sites developing and validating an improved integrated methodology of characterization based on different new statistical processing and modelling, coupled with present (and adapted) analytical and measurement methods, with respect to sustainability and economic objectives. The specific task of MTA EK in the frame of WP 5 – as the task leader of WP 5.3 – is to participate at in situ and on site initial characterizations, mapping of contaminated areas, determination of hot spots and sludge tank and hot cell measurements.

The third project is the 2nd phase of ITRAP-10+ („Illicit Trafficking Radiation Assessment Program, 2017-2019”) with the primary aim to build testing and performance assessment capacity within EU member states to improve international standardization and detection capabilities. During the project JRC provided portable spectroscopic radiation portal monitors (SRPM), handheld Radionuclide Identification Device (RID) and personal radiation dosimeters (PRD) for American National Standards Institute (ANSI) based tests for five test laboratories including MTA EK. At the end of the project the results of the measurements and the intercomparison will be discussed and analysed.

Methods

In the C-BORD project an advanced X-ray scanning system (developed by Smiths Detection), a set of relocatable and mobile radiation portal monitors (RPM, developed by Symetrica Ltd. and Commissariat à l’Énergie Atomique et aux Énergies Alternatives (CEA)) and a new design of gas phase detectors (developed at the University of Manchester and Bonn-Sieg-Rhein University) were tested at Röszke land border crossing place (Figure 1).

The next generation cargo X-ray system has been designed to improve both the accuracy and the material classification capabilities (high energy material discrimination of X-ray images). The new HCVM-T X-ray scanner, included in the trailer, is capable of operating both in portal and in mobile modes (Figure 2). These X-ray screening systems are designed to optimize security checks at ports, airports and border crossings. These systems are used to inspect entire trucks (cabin included), containers and smaller vehicles even for threats such as explosives, narcotics, weapons of mass destruction (WMDs), contraband, as well as for manifest verification, reducing the need for manual inspection. When equipped with the automatic radioactive material detection (ARDTM) (optional), the HCVM-T simultaneously carries out both the X-ray inspection and an analysis to detect the presence of radioactive gamma and/or neutron materials within the container or vehicle. The trailer is equipped with an electrical engine that effectuates independent forward and backward motion. The HCVM-T series systems use a range of accelerators from 4 MeV to 6 MeV, allowing steel penetration ranging from 280 mm to 320 mm, while providing a high throughput of up to 25 trucks per hour in scan mode and up to 150 trucks per hour in pass through mode, with up to 4 system operators in the cabin.
The current version of RPMs is a new generation of passive neutron and gamma detection systems used both in mobile and relocatable arrangements (Figure 3), designed to detect radioactive and nuclear materials. The main aim of the passive technology development is to achieve better sensitivity and improved isotope identification. The new design is capable of determining the category of the radioactive material and its position in the cargo. During the field validation exercises two types of RPM systems, integrated with a HCVM-T X-ray system (Figure 1), were tested by using various radioactive and Naturally–occurring Radioactive Materials (NORM) (e.g. fertilizers). Besides this SRPM system, similar gamma and neutron detectors were located in a passenger car and were used during the field exercise to test both mock-up containers and commercial trucks.

The INSIDER project started during the last quarter of 2017. MTA EK’s first task was the identification of European companies’ methodologies for radiological characterization of nuclear installations undergoing decommissioning and gathering information about instruments and methodologies in use for radiological characterization of contaminated sites and structures in constrained environment (high temperature and/or humidity, dose rate, etc.). The experimental work started in Q3 2018. In the frame of an INSIDER based international intercomparison exercise the gamma spectrometry experts of MTA EK carried out waste characterization measurements at the partly decommissioned zone, i.e. at the concrete wall of the biological shielding of the BR-3 type research reactor of SCK-CEN in Mol, Belgium. The high resolution gamma spectra were taken with Canberra GL2020 HPGe detector. Dose rate and total gamma measurements were also performed at the sampling locations using Berthold LB-124, Thermo Scientific RadEye B20-ER and LaBr₃ instruments (Figure 4).
Concerning the **ITRAP+10** project, the testing of the radiation detectors SRPM, a RID and an PRD (Figure 5) was performed at the Testing Laboratory of MTA EK according to the relevant international standards (e.g. ANSI4243) using the required gamma and neutron radiation sources (Special Nuclear Materials (SNM), NORM, medical and industrial isotopes). The Testing Laboratory consists of two rooms, both equipped for different types of testing applications (Figure 6 and 7).

![Image of instruments](image1)

### Figure 5: Three categories of instruments taking part in the round robin exercise

**PRD**

**RID**

**Pedestrian SRPM**

![Image of test beds](image2)

**Figure 6: Dynamic test bed facility at MTA EK with the SRPM detector under test**

![Image of test beds](image3)

**Figure 7: Static test bed facility at MTA EK with the PRD detector under test**

### Results

1. As a conclusion of the **C-BORD** field validation exercise at Röszke it was found that the next generation cargo X-ray system of SmithsD with improved accuracy (of the X-ray images) and material classification capabilities (high energy material discrimination) has come up to the expectations. Similar conclusions were drawn with respect to the high level
performance of the Symetrica designed mobile, portable, built-in and fixed portable monitors. The CEA designed fixed radiation portal monitor has also shown good performance. Only the gas phase detection technology was evaluated as promising but needing further development.

The idea of combining detection technologies to maximize effectiveness and efficiency was achieved by developing the common user interface, which allows better allocation of human resources and also facilitates to shorten the time of the customs inspections. This is with no doubt one of the biggest benefits of the C-BORD project.

It was also concluded, that customs organizations need more technology support for the control of non-commercial traffic and private vehicles.

2. In the frame of the INSIDER project high resolution gamma spectrometry measurements have been performed by MTA EK to characterize the concrete shielding of the decommissioned reactor zone. The high resolution HPGe gamma spectrometry measurements revealed the presence of $^{154}$Eu and $^{60}$Co as main components and $^{152}$Eu, $^{137}$Cs and $^{133}$Ba as minor components in the samples. Dose rate and total gamma measurements were also performed at the sampling locations. The evaluation of the measurements as well as the comparison of the data measured by the other participants are in progress.

3. Summarizing the main results of ITRAP+10 project it was concluded, that most of the planned tests could be performed at the MTA EK Detector Testing Laboratory, though some modifications had to be made on the testing facility itself, or the test methods, in order to meet the test requirements on a satisfactory level.

Remaining work

1. The C-BORD project has been completed and finished in 2018. Further continuation of the work, maybe in the frame of another international project, is under review and investigation.

2. The INSIDER project is continued according to the present programme and milestones. Waste characterization measurements by MTA EK will also be performed at another partly decommissioned research reactor in Ispra, JRC.

3. The final report of the ITRAP+10 project is under preparation and the project will be completed and finished with a final evaluation meeting in 2019.
UNCERTAINTIES OF ATMOSPHERIC DISPERSION CALCULATIONS

Csilla Rudas, Péter Szántó, Tamás Pázmándi

Objective

The objective of the CONFIDENCE research project is to understand, reduce and cope with the uncertainty of meteorological and radiological data and their further propagation in decision support systems, including atmospheric dispersion, dose estimation, food-chain modelling and countermeasure simulation models. Work package 1 (WP1) is focused on modelling of uncertainties during the emergency phase, from meteorological and source term inputs, and applied to atmospheric dispersion calculations and dose estimations.

Methods

In the second year of the 3-year long EU H2020 project, the input and model parameters used in the atmospheric dispersion calculations were selected based on the uncertainty evaluation done in the previous year. First, a simple deterministic calculation was performed by all participants testing the use of meteorological data and producing the results in a common form. After the simulation programs were tested, the calculations for the Borssele case study (a hypothetical radioactive release from the Borssele nuclear power plant) were carried out. In this release scenario the source term and meteorological uncertainties were investigated. The source term uncertainties included time to release (24 h +/- 6 h, equally distributed), the effective release height (50 m +/- 50 m, equally distributed) and the released activity (factor 1/3 to 3). The meteorological uncertainties were considered with meteorological ensemble data provided by the Harmonie-AROME model with a horizontal resolution of about 2.5 km and a temporal resolution of one hour. The time-span of the data was 72 hours and the domain was 300 km x 300 km.

Results

The results of the participants are shown on maps of probability of threshold exceedance, based on an ensemble of simulations and corresponding to the probability that a given zone is contaminated above a given level. The reference levels in this project were:

- 10 kBq/m² deposition for Cs-137 and I-131;
- 10 mSv effective dose for 1-year old child;
- 10 mSv inhalation thyroid dose for 1-year old child.

Based on these thresholds, useful outputs for decision making are the maximum distance and surface area affected by the threshold exceedance and associated uncertainties. The probability maps of threshold exceedance for deposition of Cs-137 are shown in Fig.1 for three participants. In this figure, the variability between the results given by the participants is clear. The pattern induced by scavenging, showing “hot spots” of deposition, is clearer in Participant #2 and Participant #3 maps, while the results of Participant #1 show a more continuous plume.

Figure 2: Probability maps of a threshold exceedance of 10 kBq/m² for Cs-137 deposition, for a number of discrete bands of percentiles, for several participants [1]

Remaining work

Further calculations will be conducted for the Western Norway and Fukushima release cases, as well as an additional Borssele simulation focusing on a different meteorological situation with higher uncertainties. Recommendations will be made for the use of uncertainty analysis and propagation with an ensemble approach in an operational context. In the last year of the project, the results of all the simulations will be evaluated and the findings will be presented in deliverable documents and at a dissemination workshop.

Related publication

Detector Development for the European Spallation Source

Eszter Dian, Milán Klausz, Péter Zagyvai

Objective

The European Spallation Source (ESS) aspires to be the brightest neutron source of the world, which requires joint and organised efforts of the neutronic community, as well as research and development in fields like neutron instrumentation, especially detector development, in order to meet the potential of the ESS. In addition, the recent ³He-shortage necessitates the development of new, ³He-replacement neutron detectors where it is reasonably achievable. As part of this effort, the investigation and development of two, novel solid ¹⁰B₄C-converter-based, Ar/CO₂-filled detectors were planned; for the off-the-shelf BCS (Boron Coated Straws) detector, and for the Multi-Grid detector, jointly developed by the ESS and the ILL (Institut Laue-Langevin).

Methods

Thanks to the recent development of neutron simulation tools, detailed and realistic GEANT4-based Monte Carlo simulation studies were performed for both detectors. A comprehensive study of the BCS was presented, investigating various aspects of the detector performance, e.g. efficiency, activation, absorption and the impact of scattering on the measured signal. This detector has already been selected for one of the Small Angle Neutron Scattering (SANS) instruments of the ESS, for which the exceptional flux of the ESS challenges the count-rate capability of the detector. Therefore, the BCS detector was also modelled under realistic operating conditions of the ESS SANS instruments.

A similar model was built for the Multi-Grid detector as well, which will serve the chopper spectrometers of the ESS. These instruments, since they are based on inelastic neutron scattering, are particularly background-sensitive, and a large Signal-to-Background Ratio (SBR) is a key requirement for them. For this reason, sources of intrinsic scattered neutron background for the Multi-Grid detector were determined and studied separately, and for the first time, thermal neutron scattering background sources were modelled in a detailed simulation of detector response. Based on the results obtained, optimisation of the internal detector shielding was started in order to increase the SBR via background-suppression.

Results

For the BCS detector, the detection efficiency was determined for representative incident neutron energies in multiple detector-system setups, and recommendations are made for a multi-panel design. The absorption and activation of the structural materials are found to be sufficiently low, as well as the scattering effects for SANS applications. The simulations revealed the limitations the detector choice is subjected to and provided valuable input for the decision-making process of the final detector design.

Figure 1: Peak incident rate per BCS straw for realistic worst-case scenario for SANS instruments at ESS

The Multi-Grid detector model was validated against measured data from previous detector tests, being part of the overall validation of the used simulation framework. The comparison of the impact of scattering on different detector and instrument components emphasised the importance of the intrinsic detector background, providing input for further design optimisation for background suppression.

Remaining work

The detector count rate study is a three-year project. Specific simulations are going to be performed for the BIFROST instrument of the ESS in the remaining one year.

Related publications

ENGINEERING AND NEUTRONIC DESIGN OF AN EXPERIMENTAL CAVE FOR THE EUROPEAN SPALLATION SOURCE

Szabina Török, Péter Zagyvai, Milán Klausz, Viktória Sugár

Objective

The focus in this part of the project is to find engineering solutions of Neutron Macromolecular Diffraction (NMX) Experimental Cave, which is to be built as part of the European Spallation Source (ESS) in Lund, Sweden. The experimental cave provides biological shielding to personnel standing outside its walls while the neutron shutters allow the beam inside the cave. The cave also provides a reduction of background radiation reaching the detectors inside the cave.

Methods

Based on a complex requirement system provided by the ESS, the cave has to comply with numerous requirements like radiology, stability, functional as well as manufacturing and transport related constraints. This year, the main objective of the project was to present the mechanical design of the system and to demonstrate its capability to fulfil the requirements and comply with the engineering constraints. The compliance will have to be proved by a complex 3D model, multiple radiology Monte Carlo N-particle Transport Code (MCNP) simulations and structural engineer’s statement.

Results

The existing model is a result of development, where the model had gone through several versions before reaching current design (Figure 1). The cave walls and roof are a reinforced concrete structure assembled from premanufactured units of 90 cm thickness. This bulk is necessary to protect the users from radiation emerging in the cave.

Concerning the layout, the basic shape is an ‘L’, which is designed to contain a labyrinth to protect the entrance door which is located in front of the labyrinth. It can be accessed from a separate landing structure equipped with lift for pallets and stairs. There are two separate concrete beams to support the robot rails which are designed to bear the loads of the robots moving the detectors inside the cave.

The chicane of the walls and slabs are needed to comply with the neutronic design requirements of chicane geometry and overlapping of elements. The roof is constructed of two layers, both are supported by the walls. The floor cable inlets are also designed as chicanes. They are situated under the first row of wall units connecting to the floor. The cables are then bended upstream, for which the floor slabs of the cave have openings next to the wall. The floor slabs next to these openings are not exceeding 1,5 tons thus the internal crane can be used for moving them if re-cabling is necessary.

![Figure 1: Representative networks of cluster 1 and 2](image.jpg)

Remaining work

The project is to be continued with the detailed design of the cave.

Related publication

**Concrete Activation Study for the European Spallation Source**

Eszter Dian, Katalin Gméling, Dávid Hajdú, Péter Zagyvai

**Objective**

The European Spallation Source (ESS) aspires to be the brightest neutron source of the world, which requires joint and organised efforts of the neutronic community, as well as research and development in additional fields like radiation shielding.

A new PE-B4C-concrete (polyethylene, boron-carbide) has been developed as part of the SINE2020 project, to improve the neutron absorption effect of concrete for neutron energies below 10 MeV, where iron has resonances in the cross section. It is essential to know the activation of the shielding material, like the concrete and metal components, considering both short-term effects on personnel during the operation phase, and long-term effects in the decommissioning of the ESS facility. Two other types of concrete samples were irradiated along with the PE-B4C samples: the “reference” concrete - a standard concrete from which the PE-B4C version was developed, - and the “Skanska” concrete. The double aim of the current study is to compare the neutron activation properties of the new PE-B4C-concrete to those of the reference concrete, and to determine the impact of the trace elements on the generated activity and recommend concrete compositions for conservative Monte Carlo activity simulations, that involve relevant trace elements in addition to the nominal composition, provided by the manufacturer.

**Methods**

For the shielding activation study, typical shielding concrete samples were irradiated in the fast and the rotating vertical irradiation channels of the Budapest Research Reactor for neutron activation analysis (NAA). The gamma-rays emitted by the samples were then measured with an HPGe detector, from which their activity and composition was determined. The chemical composition of the samples was also determined with X-ray fluorescence (XRF) and prompt gamma activation analysis (PGAA). The measured activities were compared to the results of Monte Carlo N-Particle Transport Code (MCNP) activation simulations based on the measured and nominal concrete composition data, respectively.

**Results**

The activation experiment confirmed that the newly developed PE-B4C-concrete is not activated as much as the initial reference concrete, but the study also revealed the importance of trace elements in terms of activation. A recommended, effective composition was developed for more detailed and conservative MCNP simulations, of the three studied concrete samples.

**Remaining work**

A summarising publication is in progress on the impact of concrete trace elements in neutron-generated activity.

**Related publication**

TRANSNATIONAL ACCESS WITHIN THE EC H2020 IPERION CH PROJECT

Zsolt Kasztovszky1, László Szentmiklósi1, Zoltán Kis1, Ildikó Harsányi1, Adél Len1,2, Katalin Bajnok2, György Káli2, Imre Kovács2, Zoltán Szőkefalvi-Nagy2, László Rosta2, Veronika Szilágyi1

1Centre for Energy Research, 2Wigner Research Centre for Physics

Objective

Within the IPERION CH H2020 project, transnational access is offered for experts of Heritage science to use the instruments of the Budapest Neutron Centre. In the short term experiments available there, compositional and structural data are obtained non-destructively, and information regarding provenance, condition, and genuineness of the objects are obtained.

Methods

Prompt Gamma Activation Analysis (PGAA), Prompt Gamma Activation Imaging (PGAI), Neutron Activation Analysis (NAA), Neutron Radiography (RAD), Time of Flight Neutron Diffraction (TOF-ND), Small Angle Neutron Scattering (SANS) and complementary Proton Induced X-ray Emission (PIXE) measurements can be applied for.

Results

In 2018, 14 experimental proposals have been completed. Four experiments were done to determine the chemical composition of historical glass from Roman, Byzantine and Medieval ages, in order to identify the producing workshops. Four proposals aimed to study the composition (PGAA) and the microstructure (RAD) of Neolithic and Renaissance pottery. One proposal aimed to characterize the production techniques of Bronze Age belts; one dealt with Celtic coins, and two were about the provenance of chipped stone raw materials, such as flint and obsidian. One proposal was submitted to study the salt absorption properties of various porous building materials.

Highlight: Analysis of Celtic silver coins from Slovenia - Žiga Šmit, Faculty of Math. and Physics, University of Ljubljana

Celts started to mint iron coins by the 2nd c. BC, following the Greek nominal coinage system. Beside tetradrachms, many small coins were in circulation, which are frequent finds in the eastern Alps. Prior analyses showed that the silver content for two important sites, Magdalensberg (Austria) and Celje (Slovenia) differ. 74 coins were measured with PIXE and PGAA. Kernel density estimates (KDE) from PGAA show that, contrary to the PIXE results, the coins contain varying proportions of silver, between 50 and 90 m%. The difference between the PGAA and the PIXE results has to do with the fact that the PIXE method only samples the surface material, while the PGAA method samples the whole volume of the object. For a few coins, in-beam NAA was made to determine the gold content at the trace level. The silver content distribution, obtained by PGAA is double-peaked and dominated by two coin types, with rosette and with horse motifs. One peak corresponds to coins with a base-silver core of about 50 m% Ag, while the other contains silver of about 80 m% Ag. The two different types exhibit similar silver purity distributions, which reflects two different recipes of making silver alloy formulas.

Related publications

COLD NEUTRON MODERATOR DEVELOPMENT AND COLD SOURCE UPGRADE PROJECT AT BUDAPEST RESEARCH REACTOR

József Janik, László Rosta

Objective

The European Spallation Source AB has developed the novel concept of so-called low dimensional neutron moderators. Monte Carlo Simulations have shown that this concept can improve the performance of the facility (measured in moderator brightness) by a factor of two to five in comparison to conventional volume moderator designs. On the one hand, our objective in joining this activity was to contribute to moderator developments based on the experimental possibilities of the liquid hydrogen moderator operating at BRR; and on the other hand, to design a new vessel for the BRR (Budapest Research Reactor) cold neutron source (CNS) and also to prepare the manufacturing plans for the complex up-grade of this CNS.

Methods

This activity was a part of the H2020 BrightnESS project and ran on several lines. The first step was to perform a reactor simulation on BRR including the CNS. MCMPX (Monte Carlo Method particle extended) was used to calculate the neutron and gamma field of the core, and then the calculation was extended to the moderator cell. The shape of the moderator cell was optimized by iterating for the best neutron brightness at the vessel exit and these results were used as input for the thermal-hydraulics investigations. Throughout the calculations, it was considered that the cell should be filled by para-hydrogen at as high as possible ratio with respect to ortho-hydrogen.

Our experimental approach was to measure the para-hydrogen content in the currently used CNS cell. For this case, the CNS should have run without reactor-on power, since the ortho-para equilibrium below 30K° starts shifting toward the para-hydrogen state and it will fill the cell. This process is labelled as precooling. The result of this regime modification was that the level of neutron brightness was increased as it was measured by SANS (Small-angle Neutron Scattering).

Results

Results of the simulations:

1. The optimization has shown that a low dimension type bare moderator cell has a two times higher neutron brightness than the existing cylindrical volume moderator vessel. The parameters of the low dimension type bare moderator cell were varied in the following range: radius 10-25 mm, length 90-180 mm. The moderator cell is filled with pure para-hydrogen during the optimization.

2. The applicability of a pre-moderator material was also studied. Using light- and heavy water as material of a pre-moderator could increase the neutron brightness for a low dimension moderator bare cell by 6-8 %.

The low dimension type bare moderator cell is very sensitive to the type of filling material. The high level of para-hydrogen purity in the low dimension type moderator cell must be maintained for all periods of the reactor cycle. Otherwise the neutron brightness decreases below the level which can be reached by the thick moderator. When the para-hydrogen ratio is less than 90% the thick moderator cell has better neutron properties.

Results of the measurements:

A series of pin-hole camera time-of-flight measurements were carried out to understand the possible improvement of our current brightness with the neutron moderator cell, so we can modify the ortho-para hydrogen ratio in the moderator cell. Although the measurements were not fully convincing about the geometrical effect of the low dimensional moderation (non-adequate geometry), the positive outcome was that we found a new working regime for the operation with a considerable gain in flux from the current CNS.

Plans for manufacture:

The design of a low dimensional moderator cell was elaborated and the optimal manufacturing technology is being developed. We found two methods: one is the 3D metal printing; the other is the electron beam welding. Both methods are under test.

Remaining work

A new test equipment is being considered at the reactor hall. We are going to use this experimental bench for testing the new moderator cell. It requires, however a careful redesigning of the biological shielding of fifth and fourth channels in the reactor hall.

Related publications


PARTICIPATION IN THE ACTIVITIES OF THE MULTIDISCIPLINARY EUROPEAN LOW DOSE INITIATIVE

Balázs Madas

Objective

MELODI (Multidisciplinary European Low Dose Initiative) is a European radiation protection research platform with a focus on research on health risks after exposure to low-dose ionising radiation. MTA EK is one of its members since 2013. A major activity of MELODI is the establishment and updating of a long term (>20 years) Strategic Research Agenda (SRA) for research on low dose risk for radiation protection in Europe. The SRA is intended to guide the priorities for national and European research programmes and the preparation of competitive calls at European level.

In October 2017, the European Commission indicated its intention to open a EURATOM call that includes radiation protection. The proposed work programme included topics NFRP-2018-8 for research and NFRP-2018-9 for review of previous activities. NFRP-2018-8 specifically indicated that a ‘Gap analysis’ will be required for each proposal. Therefore, the preparation of a gap analysis was a specific objective for 2018.

Methods

A dedicated working group (WG) for the development of the SRA has been formed in 2014 with one member from MTA EK. Since then, the WG regularly updates the SRA based on new findings and newly identified research needs. The WG meets once or twice a year. Since 2016, the European Radiation Protection Week series has been providing input and an open forum for discussions on the MELODI SRA. In 2018, a series of dedicated Workshops on different topics was also launched.

For the gap analysis, the WG reviewed relevant EURATOM research undertaken in Framework Programmes 6 and 7 (FP6, FP7) and Horizon 2020 (H2020) identifying their relevance to the six key areas of research identified in the MELODI SRA and roadmap: (1) To explore the shape of the dose-response relationship for radiation-induced health effects; (2) To understand the potential impact of individual susceptibility on radiation-induced health effects; (3) To identify, develop and validate biomarkers for exposure, early and late effects for cancer or/non-cancer diseases; (4) To explore and define the role of epigenetic modifications in radiation-induced health effects; (5) To explore the roles of specific target cells for radiation-induced late developing health effects; (6) To understand the health effects of inhomogeneous dose distributions, radiation quality and internal emitters.

Results

A three-day-long MELODI Workshop on Individual Radiosensitivity and Radiosusceptibility was held in Malta in March. Sessions were organized in three topics: Clinical and epidemiological observations, Mechanisms involved in radiation sensitivity, Screening systems. On the last day, there were synthesis sessions in order to prepare position papers in each topic.

The 3rd European Radiation Protection Week was held in Croatia in October. On the first day, a plenary session was devoted to presenting the results of the workshop on individual sensitivity. MTA EK was strongly involved in the session entitled “Understanding the health effects of inhomogeneous dose distributions, radiation quality and internal emitters (incl. Space)” as one of the co-chairs and one of the presenters had come from MTA EK.

The review of relevant EURATOM research surveyed the identification of gaps that were considered as potential areas for research under NFRP-2018-8 call. A mature reflection and identification of knowledge gaps would require results of all projects to be available; this has not been possible in all cases as some projects have not come to completion yet. There have been many projects supported under FP6, FP7 and H2020 that address issues highlighted by MELODI as key areas requiring research to improve low dose and low dose rate radiation health risk assessment. All funded projects align with one or more of MELODI’s key areas as identified in the SRA and roadmap. All have contributed to advancement of the field and building the scientific evidence base for low-dose/dose-rate risk assessment. All diseases/health effects of actual and potential relevance to low dose risk (cancer, circulatory disease, cognitive effects and cataract) have been considered and a shift in emphasis amongst funded projects towards the non-cancer diseases could be seen. While all projects have made progress in building the evidence base, there remain areas where additional work could be beneficial; these are considered in the gaps described in the MELODI Statement 2018. The WG anticipated that its gap analysis was going to be of benefit to those applying to the calls. The gap analysis was presented in different meetings including the European Radiation Research 2018 conference held in Pécs [1].

Remaining work

A revision of the SRA is due in 2019. Manuscripts of the position papers on individual sensitivity are to be finalized in early 2019. MELODI Workshops on non-cancer effects (2019) and on the effects of inhomogeneous exposures (2020) have to be prepared. The latter will be held in Hungary with strong involvement of MTA EK.

Related publication

II. RESEARCH AND DEVELOPMENT RELATED TO NUCLEAR POWER PLANTS
PREPARATION OF THE FUROM 2.2 CODE VERSION

János Gadó, Ágnes Griger, Katalin Kulacsy

Objective

The FUROM code had been developed in the institute about 20 years ago for the analysis of fuel behaviour in VVER-440 reactors. It was further improved using up-to-date results of measurements and state-of-the-art models. As a consequence, several official versions were released over the years. Now the version FUROM 2.2 is under preparation. The aim is to refine the modelling of fuel swelling, densification and other phenomena, to make it possible to apply the code for VVER-1200 calculations and also to perform minor corrections. The new official version FUROM 2.2 will be issued by September 2019.

The work is financed by MVM Paks NPP Co.

Methods

New models are selected based on extensive review of the literature and the available experimental data. Then they are built in and tested. Bug fixes constitute an important part of the work as well. Special attention is given to increase the transparency of the code for future programmers. The code documentation (model description, programmers’ guide and users’ guide) will be upgraded and the validation will be repeated.

Results

In 2018 the modelling of fuel swelling was studied. The new code version allows for using a conservative and a best estimate dependence of swelling on fuel burn-up, and a more detailed model that takes into account the swelling of the pellet matrix due to solid fission products is also made available. New densification models were also introduced. One of them is based on the temperature dependence of densification rather than on the burn-up dependence. A new model has been introduced to describe the growth of UO₂ grains. The model of high temperature recrystallization has been corrected. The code results with the various models will be compared to experiments in 2019. Furthermore, the calculation of VVER-1200 fuel was also made possible, though certain correlations have still to be established using reactor physics codes.

The calculation speed was basically improved in connection with avoiding the repetitive calculation of power and burn-up distributions in the pellet. Various solutions were applied to decrease the memory need of the code and to introduce mnemonic simplifications.

A summary description of the FUROM code was published [1].

Remaining work

Further model improvements have to be finalized. Validation of the code has to be performed. The new documentation has to be prepared.

Related publication

DEVELOPMENT OF ADVANCED METHODOLOGIES AND MODELS FOR FUTURE STRUCTURAL INTEGRITY CALCULATIONS

Tamás Fekete, Dániel Antók, Levente Tatár

Objective

The final objective of the research program is to develop a unified, coherent analysis methodology and also advanced models for future nonlinear SI calculations of various safety relevant systems of Nuclear Power Plant (NPP) units.

The main research directions of the program are formulated as follows:
- Large deformation models for analyses of engineering structures;
- Complex constitutive models for future engineering SI problems;
- Advanced assessment methods for evaluations of material tests;
- Long-time ageing of RPV structural materials.

For details see the EK Annual Report 2017, page 33. Methods

In the theoretical part of the project, a material model development - based on a systematic theoretical study - is being conducted in order to elaborate a state-of-the-art theoretical and simulation method that seems promising for applications in future industrial SI projects. In the modelling part, numerical models are being developed for special research problems first. These models will be further developed for industrial applications.

Results

The main goal during the theoretical part of the project was the elaboration of a complex material model that is able to describe plasticity and damage in a coupled fashion. Large deformation plasticity theory is used to model the effects of geometrical nonlinearities. Plastic-damage material behaviour is modelled in many instances by the Gurson–Tvergaard–Needleman (GTN) material model. The GTN model is based on the hypothesis that the impairment caused by void nucleation and growth in a metal may be macroscopically described by extending the von Mises plasticity theory using one scalar damage variable. Despite the fact that when using the GTN model one is able to follow the weakening of elastic-plastic metallic materials on a qualitative level, the model has some weaknesses. Among these, and one of the most problematic, is the overly simplistic model used for the description of damage evolution. Based on lessons learned from earlier numerical works and extensive literature studies, the GTN model has been redesigned. The new model is called the modified GTN model below. The central part of the modified GTN model, the plastic potential, is of the form:

$$\Phi(T, \sigma_m, d, f) = \frac{\sigma_m^2(T)}{\sigma_m^2} + 2q \cdot d \cosh \left( q \cdot \frac{\text{tr}(T)}{2\sigma_m} \right) - (1 + (q \cdot d)^2) = 0$$

where $T$ represents the Cauchy stress tensor, and $\sigma_m$ designates the local, equivalent von Mises stress. The yield stress of the matrix material is designated by $\sigma_m$, $d$ denotes the mesoscopic damage variable, and $f$ represents the microscopic or equivalently called microlocal – damage variable in the matrix material. The parameter $q$ is called the damage-mechanical coupling parameter, and $q_1$ is called the triaxiality parameter, and has the same form as in the original GTN model. Originally, $q_1$ and $q_2$ were introduced by Tvergaard to improve the behaviour of the model for larger values of $f$. Here, $q_1$ plays a slightly modified role compared to that in the original model, while $q_2$ has the same form and meaning as in the original GTN model. The evolution equation for the mesoscopic damage variable $d$ is formulated in this model according to the theory of weakly nonlinear –diffusive– internal variables in the internal variable approach of irreversible thermodynamics, as follows:

$$\dot{d} + a \nabla \cdot (b \nabla d + c \nabla d) = \dot{f}$$

where $\dot{}$ denotes time derivation. The source term for the mesoscopic damage evolution is the evolution rate of the microlocal damage growth associated (1) with plastic strain rate in the matrix $\dot{f}_{\text{mat}}$; (2) with a number $(i)$ of smaller, transient accelerations? of damage, – each of them causing faster, but not final, catastrophic weakening in the material at around distinct critical values of $\varepsilon_p$ (designated as $\varepsilon_{p;i}$) – called $\dot{f}_{\text{crit};i}$, and (3) with the jump-like acceleration of microlocal damage, – at $\varepsilon_{\text{crit};i}$ – called $\dot{f}_{\text{final}}$, causing the final, fast stability loss of the material:

$$\dot{f} = \dot{f}_{\text{mat}} + \sum_{i} \dot{f}_{\text{trans}} + \dot{f}_{\text{final}} = (1 - f) \cdot \dot{\varepsilon}_p + \sum_{i} A(e_{\text{crit};i}) \cdot \dot{\varepsilon}_m + B(e_{\text{crit};i}) \cdot \dot{\varepsilon}_m$$

where $\varepsilon_p$ designates the plastic strain tensor, and $\dot{\varepsilon}_m$ denotes the equivalent plastic strain as follows:

$$\dot{\varepsilon}_m = \frac{2}{3} \varepsilon_m : \dot{\varepsilon}_m, \varepsilon_m = \int_0^\tau \dot{\varepsilon}_m d\tau$$

It is assumed that during a transient acceleration of microlocal damage, the kinetics of the phenomenon may be characterized with a normal distribution around $e_{\text{crit}}$; therefore, $A(e_{\text{crit}})$ is defined as:

$$A(e_{\text{crit}}) = \frac{f_i}{\sqrt{2\pi(s_i)^2}} \exp \left( -\frac{(e_m - e_{\text{crit}})^2}{2(s_i)^2} \right)$$

For details see the EK Annual Report 2017, page 33.
where $\varepsilon_{\text{crit}}^i$ denotes the critical value of $\varepsilon_m$ at the $i$-th critical step, $s_n^i$ means the standard deviation of $\varepsilon_m$ around $\varepsilon_{\text{crit}}$, and $f_n^i$ designates the weight factor (which describes the influence of the process on the microlocal damage evolution rate). It is assumed in the description of the final failure that the jump-like acceleration of the microlocal damage may be characterized with a three parameter Weibull distribution around $\varepsilon_{\text{crit}}^{\text{final}}$; therefore, $B(\varepsilon_{\text{crit}}^{\text{final}})$ is defined as:

$$B(\varepsilon_{\text{crit}}^{\text{final}}) = \alpha \cdot f_n^{\text{final}} \cdot \left(\frac{\varepsilon_m - \varepsilon_{\text{crit}}^{\text{final}}}{s_n^{\text{final}}}\right)^{\alpha} \exp\left(-\frac{\left(\varepsilon_m - \varepsilon_{\text{crit}}^{\text{final}}\right)^{\alpha}}{2s_n^{\text{final}}^{\alpha}}\right)$$

where $\varepsilon_{\text{crit}}^{\text{final}}$ denotes the critical value of $\varepsilon_m$ at final failure, $s_n^{\text{final}}$ is the scale parameter, $\alpha$ is the shape parameter of the distribution, and $f_n^{\text{final}}$ designates the weight factor (which describes the influence of the process on the microlocal damage rate). According to preliminary calculations for the evolution of the mesoscopic damage variable $d$, the modified GTN model will be able to simulate the ‘multi-stage’ character of load carrying capacity attenuation, observed on many materials, including structural steels. Based on the results, a typical example showing the nature of the evolution of the mesoscopic damage variable $d$ during steady, extremely slow stretching is depicted in Fig. 1. The material model will be incorporated into user defined subroutines available in the MSC Marc FEM system.

![Diagram showing the multi-stage character of damage evolution, according to the modified GTN model](image)

In the modelling part of the project, the calculation methodology that simulates the ballooning tests of fuel cladding tubes has been further developed based on a geometrically and materially nonlinear formulation of the problem. Thermomechanics, employing large deformation plasticity, was used to model the effects of geometrical and material nonlinearities that are present in the system during calculations. The temperature dependent plastic flow curves of structural materials have been developed from tensile test results, performed at many temperatures. Numerical calculations were performed using the MSC Marc FEM code. During the process, a parametric study was conducted to assess the influence of material inhomogeneities on the test results, because – based on theoretical considerations – it was expected that material inhomogeneities can have strong effects on the final state, more specifically on the geometry and on the stress-strain state of the test piece.

The 3D finite element models of the ballooning specimens have been tested. The final shapes of some specimens are shown on Fig. 2. The simulations have been performed on a geometrically perfect tube model, with an assumed flat material inhomogeneity (see Fig. 3. a). The calculation results for the total equivalent plastic strain at the last calculated time step are presented in Fig 3. (b). It can easily be seen that the geometrical shape of the specimen evolves into a pronounced asymmetric 3D structure, which is very similar to the shape of the tested specimens. The calculated results for the temperature distribution can be seen on Fig. 4. (a), while the results for the equivalent von Mises stress distribution at the last calculated time step are presented in Fig 4. (b).

Based on the improved theoretical and numerical results, it can be stated that the more complex models provide a deeper understanding of the events occurring during the material tests, as well as contributing to the development of more advanced models for future SI calculations of fuel cladding tubes.
Figure 2: Fuel cladding tube pieces after the ballooning tests

Figure 3: FEM model of a tube piece with flat initial material inhomogeneity distribution (a), final results –shape and equivalent plastic strain field– of the ballooning simulation (b)

Figure 4: Final FEM model results for the ballooning simulation of a tube piece: temperature field at the final stage (a), and equivalent von Mises stress field (b)

The parameters of a given material model can be determined by adequate measurement procedures. A measurement procedure consists of the necessary observations and their evaluation using the very same material model. During SI calculations, the behaviour of a structure will be examined with its more complex geometrical model which is dependent on the material model of the relevant phenomena occurring in the structure during its operation. The key point for reliable calculation results is that the same material model needs to be applied to the structure model as well as to the material model used to evaluate the material tests, to meet the essential requirement that ‘the theory and the experiments need to be harmonized’. Nowadays, very simple material models are used in standard measurement evaluation procedures, but cannot be used to determine the parameters of complex material models. Advanced assessment methods for the evaluations of material tests have been developed therefore, in order to ensure that the appropriate theoretical framework is used when estimating the parameters of a material model. 3D numerical models have been developed for the evaluation of three-point bend fracture mechanics tests (see Fig. 5.a), using the MSC Marc FEM system. In parallel with the theoretical and numerical work, an optical data acquisition and data evaluation system has been developed and tested, with the aim of supporting the measurement evaluation process with more detailed and accurate geometrical data. A representative picture of a specimen during a three-
point bending test is presented in Fig. 5 (b). Combining the high-performance, computing assisted, measurement simulations with more accurate geometrical data registered during the tests, paves the way to extract more reliable data from the measurement procedures for future industrial calculations in the near or mid future.

Figure 5: 3D FEM model of a three-point bend fracture mechanics specimen (a), a photo made of a three-point bend fracture mechanics specimen during the measuring process (b)
**START-UP AND TRANSIENT CALCULATIONS IN TRANSURANUS FUEL BEHAVIOUR MODELLING CODE**

*Eszter Kozsda-Barsy, Katalin Kulacsy*

**Objective**

During start-up of the 30th cycle of Unit 4 of the Paks NPP a short and steep increase in power occurred. The Hungarian Atomic Energy Authority commissioned MTA EK to conduct an independent study of this event.

**Methods**

Due to the swelling of the pellet, the gap between the cladding and the fuel decreases with increasing burnup, and once it disappears PCMI (pellet-cladding mechanical interaction) occurs. During PCMI the cladding experiences stress, especially during power ramps. Meanwhile fission products cause corrosion on the surface of the cladding. The effect of stress along with corrosion may lead to stress-corrosion cracking (SCC) and crack propagation which may lead to fuel rod failure and coolant contamination. For this reason, an upper limit (SCC limit) is imposed to tangential stresses. Further quantities relevant to cladding integrity are yield stress, ultimate tensile strength and the limit of 0.5% plastic strain.

We made simulations concerning the behaviour of a VVER-440 fuel rod at 0.8 MWₑ/min and 1 MWₑ/min ramp rates with the use of the TRANSURANUS fuel behaviour modelling code and studied the effect of the power spike on the cladding. We also simulated a worst-case scenario with a significantly larger spike.

After creating input time series, we ran 12 simulations and analysed the data. The evaluation of the results was based on the limits that determine the maximum allowed stresses in the cladding during safe operation.

**Results**

The results of the simulations performed concerning the spike were compared to these limits (Fig. 1-2), and none of the limits was found to have been exceeded.

*Simulation 5: 0.8 MWₑ/min ramp rate, actual power spike*

The lines of the axial nodes 1, 2, 3, 9 and 10 are overlapping on this scale.

**Remaining work**

The project was finished as planned.
INTRODUCTION OF NEW FUEL TYPES TO THERMAL POWER PLANTS: INTERNATIONAL METHODS FOR POST-IRRADIATION EXAMINATION OF LIGHT WATER REACTOR FUEL ASSEMBLIES

Emese Slonszki

Objective
To maintain and improve the reliability of fuel assemblies and fuel elements, it is necessary to investigate and evaluate the effect of loads in the reactor on the behaviour of fuel assemblies. Therefore, we need to examine and analyse both the irradiated fuel assemblies and the individual fuel rods. This work aims to show the methods and equipment used for testing of non-leaking Light Water Reactor (LWR) spent fuel assemblies.

Methods
Part of the methods used for post irradiation examinations, such as burnup determination or geometry measurements, can be performed under power plant conditions. In the hot cells, after appropriate sample preparation, further extensive tests can be carried out, including non-destructive and destructive procedures. In this work we summarized these methods.

Results
Visual and dimensional inspections of spent fuel assemblies (FA) can be carried out even in the reactor pool. FA length, bowing and twist can be measured.

Hot cells non-destructive testing includes visual inspection (surface condition), profilometry (length, diameter, diametric and axial deformation, bow, quality), eddy current measurement (cladding integrity), interferometry (oxide thickness), gamma scanning and tomography (burnup).

Several destructive tests were also presented, like fission gas analysis (volume and composition), various microscopic techniques (pellet and cladding microstructural characterization), hot vacuum extraction and differential scanning calorimetry (hydrogen and deuterium content). In addition, techniques which are used to determine the chemical, mechanical and physical properties of the cladding were presented, like ion beam techniques as well as hardness, tensile, fracture toughness, fatigue testing and finally oxygen/metal ratio and thermal diffusivity measurements.

Spent fuels and fuel assemblies can extensively be characterized by the presented pool-side and hot cell post irradiation examination (PIE) techniques. These techniques are constantly being developed. All this contribute to the fact that the establishment and operation of a hot cell is very useful when introducing new fuel elements. This makes it possible to check and verify their safe operation.

Remaining work
This project has been completed.

Related publication
**Modelling the Breakaway Oxidation of the Russian E110 Cladding**

*Katalin Kulacsy*

**Objective**

The cladding of the fuel pins currently used at Paks NPP is manufactured from a mixture of zirconium made by the electrolytic and the iodide reduction methods. During a loss-of-coolant accident (LOCA), the high-temperature steam oxidises the cladding. Outside the temperature range of 800-1050 °C, the oxide layer is compact and inhibits further oxidation even for long oxidation periods, but within this range it repeatedly cracks and spalls off, exposing fresh metal to the steam, which results in an accelerated, so-called breakaway oxidation characteristic of this specific alloy. Traditional parabolic oxidation kinetics correlations based on diffusion through an ever thickening compact oxide layer cannot describe this phenomenon as it results in linear kinetics, therefore a new model had to be developed. The work was supported by Paks NPP.

**Methods**

The basic concept was to describe oxide spalling in such a way that at a given weight gain a certain constant surface fraction of the oxide exfoliates from the metal, and the fresh metal surface oxidises as the as-manufactured cladding. Exfoliation affects identically all parts of the surface: those that have not suffered spalling yet and those that have already suffered one or even several spalling events.

First a model was developed to describe the hydrogen production during breakaway oxidation. The model takes into account the oxidation of the metal, the partial absorption of the hydrogen produced in the process and the periodic exfoliation of a certain surface fraction of the oxide, resetting the oxidation kinetics to the initial rate characteristic of the fresh metallic surface, as described above. The parameters of the model were fitted using the results of high-temperature steam oxidation experiments carried out at MTA EK on E110 cladding in the breakaway regime, that featured a TCD (thermal conductivity detector) to measure the amount of released hydrogen on-line, in addition to measuring the weight gain at the end of the oxidation period.

Then the parameters of the model (the temperature-dependent weight gain threshold where spalling occurs and the exfoliating surface fraction) were determined using hydrogen production and weight gain measurements.

Finally, for very long term oxidation a linear kinetics correlation was fitted to the curve resulting from the detailed model.

**Results**

The measured integral TCD signals were well reproduced, which justified the basic concepts of the model (Fig. 1). The downward spikes are due to increased hydrogen absorption of the fresh metal surfaces in the simulation, but they do not affect the integral results.

The agreement between the measured and calculated weight gains was good, considering the large scatter of the measured data (Fig. 2).

Moreover, the sum of the individual parabolic oxidation kinetics yielded a near linear function, in accordance with experimental findings.

**Remaining work**

The work has been finished. Journal publication of the model is planned.

**Related publication**

ACTIVITIES OF MTA EK AS MAIN CONSULTANT OF PAKS NPP

Katalin Kulacsy

Objective
MTA EK, together with NUBIKI (Nuclear Safety Research Institute), has been the main consultant of Paks Nuclear Power Plant (NPP) for over a decade. The main consultant supports the NPP in solving safety-related technical issues and helping with strategic planning. The work is done by the most experienced and highly qualified members of the staff on the basis of yearly work plans. In 2018 MTA EK undertook the following separate tasks, done by different groups of experts:

- determination of the eye lens dose for photon radiation
- analysis of the organic material content of secondary circuit deposits
- outlining the future of structural integrity (SI)
- assessment of the on-line hydrogen measurement method in the primary circuits.

Methods
Each task required a different method, which can be summarized as follows.

In order to determine the eye lens dose, a survey of the national and international requirements, best practices and of different dosimeters applied was given. Calculations were made to justify the usability of whole-body dosimeters to determine the eye lens dose, taking into account the limitations of this solution.

Six samples were taken from different parts of the secondary circuit of Paks NPP and analysed by means of scanning electron microscopy, organic carbon analysis, dissolution tests, high-performance liquid chromatography with mass spectrometry and gas chromatography with mass spectrometry.

The future of SI was outlined based on literature survey and in-house method development.

The sources, importance and typical quantities of hydrogen in the primary circuit were reviewed on the basis of literature. The manual and on-line measurement techniques were assessed in terms of accuracy and calibration.

Results
The individual results of the tasks were the following.

The eye lens dose could be determined using whole-body dosimeters in the typical radiation fields present in Paks NPP, except for certain special cases where the dosimeter has to be worn near the eye.

The secondary circuit deposits did not contain any inorganic carbon compounds. The morphology and composition of the samples were similar, they consisted mainly of iron and oxygen. The main organic compound was the octadecylamine used as anti-corrosion coating during shut-down periods.

The outline of the future of SI presented past and present best practices and wide-spread and innovative problem solving methods, including the role and description of material aging in the assessment of the technically allowable lifetime of a structure. Modelling the effect of inhomogeneities was identified as the most important imminent task in the field.

The on-line measurement of the hydrogen concentration has a good accuracy but is not properly calibrated. A new calibration method was proposed, together with a new scheme for hydrazine feeding and alternative control procedures.

Remaining work
The 2018 tasks were finished.

Related publications


MULTI-PHYSICS: COUPLING OF REACTOR PHYSICS AND FUEL BEHAVIOUR ALGORITHMS OF THE HOT CHANNEL ANALYSIS

András Keresztúri

Objective

In the transient phase of a fast reactivity event, the heat transfer process in the hot-channel fuel pin is influenced to a great extent by the burnup and the profile of the relative power inside of the pellet. However, these characteristics are determined during the long term burnup process, in which the resonance self-shielding of the reactor physics model plays an important role. On the other hand, the resonance self-shielding is significantly temperature-dependent, and the distribution of this parameter depends on the heat transfer process, which itself is influenced by the gap size and the fission gas release. The latter parameters are outputs of the fuel behaviour modelling. Consequently, online coupled stationary-reactor physics and fuel behaviour algorithms must be applied to model the above mentioned complex phenomena correctly. However, the present practice is to separate the mentioned disciplines in an approximate manner. The goal of the present study was to quantify the effect caused by this approximation.

Methods

The main characteristics of the two algorithm types are as follows. Concerning the reactor physics, the hot fuel pin surrounded by a whole fuel assembly is modelled by using the first flight collision probability method. The hot fuel pin is subdivided into 16 cylindrical layers with equal-sized volumes. 35 thermal and 35 epithermal energy groups were used for modelling the whole assembly with the exception of the hot channel where 10 000 energy groups were used in order to model the resonance self-shielding more precisely and correctly. Concerning the fuel behaviour, the following effects were taken into account: fission gas release, densification and swelling due to the burnup, heat transfer and expansion effects, elastic and inelastic geometrical changes including the creep of the cladding, closure of the gap, and pellet-cladding mechanical interaction.

Results

The differences between the correct combined algorithm and the approximation using separate methodologies are in the range of the uncertainties of the separated algorithms. As an example, see the figure below where the burnup-dependent average fuel temperatures are presented.

Remaining work

There is no remaining work.

Related publication

INVESTIGATION OF THE REACTOR HEAT TRANSFER FUNCTION BETWEEN THE COLD AND THE HOT LEG OF THE PRIMARY CIRCUIT

Sándor Kiss, Sándor Lipcsei

Objective

In the steady state condition of the reactor, temperature inhomogeneities travelling together with the primary coolant pass through the reactor core and induce reactivity fluctuations generating small perturbations of the reactor power. This change of the power is moderated by the negative feedback of the Moderator Temperature Coefficient of the reactivity and the Doppler effect. This variation of the energy production reacts on the coolant temperature and so on the negative feedback. Additionally, due to circulation of the coolant, the perturbations arisen in the primary loop pass through the reactor core and the steam generators several times before their attenuation (more details in [1]). In this way, the perturbations passing through the core are fed back with a delay of the circulation period of the primary coolant with a significant attenuation. The complexity of these effects causes difficulties in the determination of the heat transfer properties of the primary loop.

Methods

In this research the propagation mechanism of the temperature fluctuations was investigated above 0.1 Hz using the measured hot and cold leg temperature signals of the primary loops of a VVER-440 reactor and an estimation method of the heat transfer functions of the coolant passing through the steam generators and the reactor core has been provided based on the measured temperature data.

In order to carry out this investigation some of our previous works are invoked. The investigation requires the knowledge of circulation period of the primary coolant and the transit times of the coolant between the thermocouples in the primary loops [2], the transfer properties of the steam generators [3], as well as the source and the propagation of the temperature perturbations and the proportions of the perturbation components [1]. To achieve this overall evaluation an average primary loop model was also created [1], [2], [4].

Results

An estimation of the reactor heat transfer function between the cold and the hot leg of the primary circuit was provided (see Figure 1), which was enabled by the finding that the ratio of the auto power spectral density functions of temperature noise of the reactor and the steam generators can be well approximated with the ratio of the spectra of the hot leg and the cold leg temperature noise. It was found that the effect of the control system and the power feedback cannot be neglected up to 0.2 Hz for VVER-440 reactors. The transfer properties of the steam generator were estimated using temperature noise measurements as well. For more detail see [5].

Figure 1: Frequency response of the reactor heat transfer function at 10% accuracy of the transit time

Related publications

DEVELOPMENT OF INTERACTION TECHNIQUES FOR A VIRTUAL CONTROL ROOM

B. Katalin Szabó

Objective

The objective was to implement gesture-driven and control-panel-driven navigation in the virtual model of a huge control room of a power plant, in an immersive virtual reality application, and the handling of collisions in the model.

Methods

Hardware and software tools used: Leap Motion hand movement sensor, Oculus Rift headset, 64-bit Windows 10 operating system, Blender Game Engine (version 2.76b), OpenHMD package with python-rift extension. The Leap Motion device drives a self-developed rigged hand model which reproduces the appearance and the movement of the real hands with acceptable accuracy.

First a finger-operated virtual control panel was built into the model, the buttons on it corresponded to translational and rotational movements, as if the user was controlling a wheelchair. However, this input method did not prove accurate enough, there were misses while hitting the buttons next to each other. (This is affected by how good the light conditions are, as the accuracy of the Leap Motion sensor is very sensitive to light conditions in the room.) Therefore, this line was abandoned and gesture-driven interaction ("natural interaction") was introduced, where the navigation is solely controlled by the movements, gestures of the user's hands, without any physical or virtual input tool other than the hand movement sensor.

While there are various examples of gesture-driven interaction in the literature, there is no generally usable sure-fire method. Solutions are always specific to the actual applications.

For our application, the user's actions which had to be handled were divided into 3 categories:

- navigation, i.e. "walking", "moving around" in the control room, going from one spot to the other
- head rotation, i.e. the turning of the head to look at various objects
- interaction with pushbuttons and switches (this involves collision detection)

In our case, for the navigation, four degrees of freedom (out of the possible six) seemed to be adequate: translational movement along all 3 coordinate axes and rotation around the vertical axis.

Results

For the navigation, two clearly separable input modes have been introduced:

- Translational mode: the user is able to move along the 3 coordinate axes. This is possible when only the left hand is within the detection range of the Leap Motion, the right hand is out of sight. The user moves his/her hand along 1, 2 or 3 coordinate axes, and the view moves with it. The most important direction is along the horizontal axis. As the user sometimes has to travel large distances, acceleration has been implemented. This mode ends when the user puts his/her right hand into and/or pulls his/her left hand out of Leap Motion's "sight". When the user's left hand is clenched into a fist, the movement of the hand does not result in the movement of the view – this sub-mode is necessary to make it possible for the user to return the hand into the field of detection ("sight") of the sensor.
- Rotational mode: the user is able to rotate the view around the vertical axis, by rotating his/her hand. This mode is in effect only when the right hand is within the detection range of the Leap Motion and the left hand is out of sight.

The interaction mode – to be implemented – is in effect when both hands are visible and can interact with buttons and switches. Additionally, to use the already implemented head rotation input is possible all the time. Unlike the rotational mode described above, it may occur around all 3 axes, and it affects only the user's view, not the position or orientation of the hand within the control room.

Remaining work

Implement interaction mode (handling collisions). Test the various interaction modes rigorously.
DEVELOPMENT OF AN EXAMINATION TECHNIQUE TO ANALYSE SILVER DEPOSITS (SILVER MEASUREMENT ON THE BY-PASS SYSTEM OF THE PAKS NUCLEAR POWER PLANT)

István Almási, Gergely Dósa, Zoltán Hlavathy, Zsolt Kerner, Péter Kirchknopf, András Kocsonya, Katalin Zsuzsanna Szabó, Péter Völgyesi

Objective
A measurement method was developed to determine the surface activity concentration of Ag$^{110m}$ on the tubes of the by-pass system by in situ gamma-spectrometry, to map the spatial distribution and to study the temporal changes of Ag$^{110m}$. During the project several locations of the by-pass system were measured and the dose rates were determined. The other aim of the project was to determine the physical-chemical processes responsible for the Ag$^{110m}$ transport.

Methods
Altogether 70 points were analysed by in-situ gamma-ray spectrometers and dose rate meters during the reparation period of each reactor blocks. Eight 1-week long measurement campaigns were carried out in the 3-years long project. Additionally, few weeks long gamma spectrometry measurements were also performed on a given point in order to carry out time series analysis. A calibration methodology ('tube-model') was also developed at MTA EK to determine the surface activity concentration of Ag$^{110m}$ (Figure 1).

Results
By evaluating more than 500 measurements, the dose rate and Ag$^{110m}$ activity concentration maps were completed for the 4 reactor blocks in a 3-years long period. The results enabled us to compare the amount and distribution of Ag$^{110m}$ in the different reactor blocks and also the Ag$^{110m}$ variation each year in the block studied. Significant portion of the gamma dose rate is originating from the Ag$^{110m}$ nuclide. Based on our study it was possible to identify hot spots with higher activity concentration and gamma dose rate values as well as the main parameters influencing the Ag$^{110m}$ transport. The temperature, pH and redox potential were revealed as main parameters influencing the solution/deposition processes of Ag$^{110m}$.

![Figure 1: Calibration model to determine the surface activity concentration of the by-pass system tubes developed at MTA EK. Components of the model: 1: guide rail, 2: bowl screw, 3: energy chain, 4: moving panel, 5: power supply, 6: control unit, 7: reversing trigger, 8: electro-motor, 9: bearing](attachment:image.png)

Remaining work
The project has been finished in 2018.
WORKING FLUIDS

Attila R. Imre

Objective

One of the major issues for sustainable development of electricity production is to use low-temperature heat sources (60-200 °C) like thermal solar, geothermal, biomass or waste heat. Conventional water-based thermodynamic cycles are not suitable in this temperature range or operate with low efficiency, therefore other working fluids need to be applied. These fluids are usually organic ones with low boiling point, where the given temperatures are sufficient to produce organic vapour with pressure high enough to drive generators. One of the thermodynamic cycles used for this purpose is the Organic Rankine Cycle (ORC), using organic material instead of water as working fluid. In this study, we are trying to determine how to choose the thermodynamically best working fluid for a given heat source. Elementary steps (adiabatic expansion/compression and isobaric heating/cooling) of fluids were also studied.

Methods

Analytical method, special computer codes and some commercial codes and databases (ThermoC, NIST Webbook, Cycle-Tempo) were used for the calculations.

Results

Organic Rankine Cycle (ORC) uses organic working fluids to reach higher thermal efficiency for low-temperature heat sources. New working fluids are usually found by a trial and error procedure testing chemically similar materials. This procedure is quite risky, considering the possibility of excluding the optimal working fluid; therefore a new method has been developed. A novel classification has been proposed [1] to help in choosing the most suitable working fluid for a given heat source (with given upper temperature). Theoretical considerations show that the most important factors in the classification are the interconnected isochoric heat capacity and the degree of freedom of the given molecule [2]. Based on these results, some simple rules can be given to choose potentially optimal working fluids not only for ORC processes but also for the Trilateral Flash Cycles (TFC) where vapour is produced by dropping the pressure, instead of heating [3]. A database for ORC liquids has been prepared and will be published soon.

For both of the aforementioned cycles (ORC and TFC) adiabatic expansion/compression and isobaric heating/cooling are very important parts, therefore the better understanding of these processes are crucial. Adiabatic, isobaric and the similarly important isenthalpic processes were investigated under unusual circumstances. For isobaric heating/cooling a thermodynamically interesting novel process was found, where heat can be transferred to/from a body, while the associated thermal expansion or contraction happens with zero work [4]. In another study, adiabatic an isenthalpic pressure drops were studied to model pressure changes during LOCA (Loss of Coolant Accidents) in Supercritical Water Cooled Reactors (SCWR) [5]. In connection with this study, relative location of adiabatic lines and the so-called Widom-lines (representing anomalous properties in the supercritical region) were calculated for several materials, including water [6]. Similar adiabatic and isochoric pressure drops were studied in deeply metastable water, demonstrating the need of a quantic (5th degree) volume component in the equation of state of metastable water [7].

Remaining work

A well-usable method will be developed next year to help engineers to find the proper working fluid for the available heat source. Also, related theoretical studies will be continued.

Related publications

Objective

The general objective of the project is the development of the elements of a code system for the alternative solution of core design and safety analysis of the new Paks units. This year, the specific aim was the development of codes for analysing reactivity transients of the VVER-1200 reactor.

Methods

VVER-1200 specific upgrading and input generation for the following codes:

− KARATE quasi-stationary neutronic-thermohydraulic code system
− KIKO3D reactor dynamics code
− ATHLET system thermohydraulics code
− KIKO3D-ATHLET coupled reactor dynamics - system thermohydraulics code
− TRABCO code for checking the fulfilment of hot-channel acceptance criteria.

Results

The above codes have already been successfully applied in the case of VVER-440 reactors. Unlike VVER-440 reactors, in the VVER-1200 fuel assemblies the control rod cluster type reactivity regulation is used. It made necessary to integrate our methods for solving a number of benchmarks related to the VVER-1000 reactor which is the predecessor of the new Paks units. We have upgraded and tested the programme required for the analysis of reactivity transients of the VVER-1200 reactor.

Figure 1, as an example, illustrates the nodalisation of the VVER-1200 primary loop in the ATHLET model.

Remaining work

This project has been completed.

Related publication

**Testing and Qualification of Cladding Samples for Allegro Fuel**

Zoltán Hózer, Péter Szabó, Tamás Novotny, Erzsébet Perez-Feró, Márton Király, Anna Pintér Csordás, Levente Illés, Marc Schyns (SCK-CEN), Rémi Delville (SCK-CEN), Daejong Kim (KAERI), Weon-Ju Kim (KAERI)

**Objective**

The main objective of the development of ALLEGRO gas-cooled fast reactor is the demonstration of operability of a fast neutron reactor with gas coolant. The first (start-up) core of ALLEGRO will be built with MOX or UOX fuel in 15-15Ti stainless steel (SS) cladding. The second core of ALLEGRO will use carbide fuel – (UPu)C or UC – in SiC cladding. In order to support the introduction of these cladding materials a qualification procedure is needed and representative experiments have to be carried out.

**Methods**

Qualification procedures have been proposed for the start-up and refractory ALLEGRO fuel on the basis of technology readiness level (TRL) approach.

The 15-15Ti cladding tube samples (provided by SCK-CEN) were tested in high temperature (1000 °C) helium with different impurities (methane, hydrogen, nitrogen). The load bearing capabilities of pre-treated 15-15Ti and Duplex and Triplex type SiCf/SiC samples (manufactured by KAERI (Korean Atomic Research Institute)) were tested in ring compression tests. Isothermal high temperature burst tests have been performed with 15-15Ti claddings using internal pressurization. Scanning electron microscopy was applied to analyse the microstructure of the cladding samples.

**Results**

The basic steps of qualification procedure were identified. Using the currently available information, the further needs were specified which include experimental activities, design work, development of numerical models, technology developments, establishment of fuel fabrication capabilities, irradiation in research reactors and post-irradiation examination of fuel.

The high temperature treatment of 15-51Ti cladding samples showed considerable mass increase only in case of methane impurity, due to its decomposition. In pure helium atmosphere the uptake was negligible. The load bearing capabilities of pre-treated 15-15Ti samples decreased in comparison with the as-received material. The treatment in methane resulted in brittle failure of the sample, while the other samples remained ductile. The ballooning tests proved that the 15-15Ti cladding tubes can keep their integrity at high temperatures. The failure pressure of samples tested at 960-1000 °C was above 18 MPa.

The ring compression tests indicated that the compression resistance of Triplex type SiCf/SiC cladding is much better than the Duplex ones’. The thermal pre-treatment of samples in helium with different impurities did not significantly influence the mechanical properties of cladding tubes.

**Remaining work**

The planned work has been completed.

**Related publications**


ALLEGRO Core Design

András Keresztúri, Gusztáv Mayer, István Pataki, Bálint Batki

Objective

In the recent generic ALLEGRO design status, a concept and the corresponding multi-discipline methodology had to be elaborated for the ALLEGRO core design where the target quantity DPA (Displacement Per Atom) is maximized by keeping the core design safety limits according to the fulfilment of the safety analysis acceptance criteria. The basic free parameters of the core design are the core size (number of fuel assemblies), the maximum allowed stationary power ("nominal power"), the plutonium content of each fuel assembly and the reactivity reserve necessary for the burnup.

Methods

For the fulfilment of the safety requirements, it was necessary to define and determine a function ("base function") playing essential role in the core design, which is the maximum value of the allowed linear heat rate at normal operation depending on the nominal reactor power. This function must be determined by a set of safety analyses of the most limiting initial event(s) of the Design Basis at the present cooling strategy. Based on earlier studies, the hot duct break was selected as the enveloping initiating event, assuming a single failure of the intact loop. The group constants of the assemblies depending on the plutonium content were determined by using the SERPENT code, while the target and the core design parameters were calculated by the KIKO3DMG code. The careful assembly-wise plutonium profiling was a labour-intensive part of the core design.

It is noted that the starting point of the investigation, namely the “base function” of the linear heat rate, can be changed if the cooling strategy of ALLEGRO is changed in the future, but the multi-discipline methodology elaborated here will still be applicable.

Results

The applicability of the elaborated concept was demonstrated. A total of 48 CATHARE safety analysis calculations were performed by varying the initial core power and the radial peaking factor. Using the methodology, the original CEA ALLEGRO core was successfully modified by decreasing the maximum linear heat rate but keeping the total power at 75MW in order to fulfill the safety criteria. The new core design fulfills the safety criteria for the peak cladding temperature also in case of the hot duct break transient which is considered as the enveloping initiating event. The radial power peaking factor ($k_e$) was set to the required value by using fuel sub-assemblies with different initial plutonium content and increasing the size of the core, while the reactivity reserve necessary for the burnup could be assured in parallel. The earlier proposal for the power reduction (from 75 MW to 35 MW) indicated 53% reduction in the irradiation capability of the core. In contrast, concerning the irradiation performance, the optimized core presented here proved only 26% worse than the original one but this latter one was not fulfilling the acceptance criteria.

Remaining work

The target reactivity reserve necessary for the burnup could have been more precisely met if the group constants were interpolated according to the plutonium content. During future long term operation, fuel behaviour investigations may modify the base curve.

Related publication

SIMULATION OF A STATION BLACKOUT TRANSIENT AND SPECIAL TOPICS OF GROUP CONSTANT GENERATION FOR THE ALLEGRO

Bálint Batki, István Pataki, István Panka, András Keresztúri

Objective
At the present status of the development of the ALLEGRO reactor, it is crucial to identify those parameters which are hard to calculate or measure precisely and play an essential role during normal operation or transients. One aim of our work was to extend the knowledge about the uncertainties of reactor physics and thermal-hydraulics parameters by performing best estimate plus uncertainty analyses of a protected Station Blackout (SBO) transient. Results calculated by different computer codes were compared to validate our model. Another objective was to prepare reliable homogenised cross-sections for the ALLEGRO; thus three special topics of group constant generation were investigated.

Methods
Thermal hydraulics analyses were performed using the ATHLET computer code. A simplified reactor core model was created. The inlet mass flow rate and temperature were given as functions of time, which were provided by the VUJE (Slovak Engineering Company in the field of Power Generation) and calculated using the RELAP5 code. The performed uncertainty analyses were based on the GRS (Gesellschaft für Anlagen- und Reaktorsicherheit, Köln, Germany) method. The Serpent Monte Carlo code and the KIKO3DMG (nodal reactor physics calculation code developed in the CER) were applied for the investigation of the group constants. One fuel assembly (1D) and full core models of the ALLEGRO were created. Apart from the calculation of effective multiplication factors (keff), group constants were also generated in the Serpent code.

Results
It was found that the simplification of the core model in the ATHLET, mostly the neglect of the radial heat transfer from the fuel assembly to the bypass and the structural elements, significantly increases the peak cladding temperature during the Station Blackout (Figure 1). This substantial effect is the result of the more than 250 °C difference between the coolant temperature in the hot channel and the bypass. The peak cladding temperature exceeded the melting point by 6 °C in the case of the more conservative ATHLET simulation. In addition, the sensitivity analyses highlighted that the uncertainty of the decay heat curve has the highest impact on the uncertainty of the peak cladding temperature. It should be mentioned, that a 3D core model is needed to accurately investigate this transient, but it is beyond the scope of this study [1].

Regarding the group constant generation topics, a novel finding is that keff values from the Serpent and the 1D KIKO3DMG are not correlated (Figure 2). The standard deviations of the keff from the two codes are approximately the same. These perceptions will be useful when we want to calculate the standard deviation of reactivity differences between the two codes. It was also seen that reactivity effects calculated using the KIKO3DMG code are within the statistical uncertainties of the Serpent result in the case of the 1D model. Finally, we show that the outermost ring of the shielding assemblies is negligible during full core simulations, which decreases the necessary calculation time of the KIKO3DMG by 20%.

Remaining work
There is no remaining work.

Related publication

Figure 1: Peak clad temperature during SBO [1]
Figure 2: Correlation between the Serpent and KIKO3DMG keffs

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**Legend:**
- ATHLET
- RELAP5

**Figure 1:** Peak clad temperature during SBO [1]

**Figure 2:** Correlation between the Serpent and KIKO3DMG keffs
Reactivity Analysis of the Modified Supercritical VVER-SCP Reactor Concept

György Hegyi, Gábor Hordósy, Csaba Maráczy

Objective

The single circuit, supercritical pressure GEN-IV VVER reactor (VVER-SCP) enables the use of a higher efficiency thermodynamic cycle, and is promising from the aspects of its closed fuel cycle and that it allows final disposal of the weapon grade plutonium stockpile. As there was no detailed information available in the literature on the flow paths of water in the reactor vessel, we have used the conclusions of the European High Performance Light Water Reactor (HPLWR) project on the flow scheme. The equilibrium fuel cycle of the modified VVER-SCP was developed last year. The analysis of several reactivity coefficients and the capability of safe shutdown of VVER-SCP were intended to be investigated in this year of research.

Methods

We have used the deterministic KARATE code system to calculate the VVER-SCP core behaviour. For cases, which were beyond the scope of KARATE, the MCNP Monte Carlo code was applied.

Results

We have found that the subcriticality of the reactor cannot be assured in a cold state. The problem can be solved e.g. by using $^{10}$B enriched $\text{B}_4\text{C}$ absorber instead of the currently assumed natural isotopic boron composition. The fuel temperature reactivity coefficients are similar for the VVER-SCP and VVER-440 reactors, but the water temperature reactivity coefficients are much weaker in the VVER-SCP reactor. Fuel assembly neutron transport calculations with the MULTICELL neutron transport code were performed over a wide range of water densities. The values of the infinite multiplication factor for two burnup values are shown in Figure 1.

![Figure 1: Infinite multiplication factors as a function of water density for two burnup values of a VVER-SCP fuel assembly](image)

The average water density in the nominal state of VVER-SCP is approximately 0.28 g/cm$^3$. At this density, the infinite multiplication factor hardly changes as a function of water density, which supports the extremely low absolute value of the water temperature reactivity coefficient.

The evaluation of the void coefficient was performed with the MCNP code by calculating the multiplication factor of the end-of-cycle state with nominal water density and vacuum. According to the calculations, the void coefficient is positive, so the reactivity increases with the loss of cooling water. To solve the problem, the use of a solid moderator, e.g. zirconium hydride is possible.

Remaining work

This project has been completed.
INVESTIGATION OF THERMAL INSULATION OF EXPERIMENTAL ASSEMBLY OF ALLEGRO REACTOR

István Farkas, István Tamásné Farkas, Attila Guba, Gusztáv Mayer

Objective

To test the new ceramic fuel in ALLEGRO reactor a few experimental assemblies will be loaded into the first mixed oxide (MOX) or uranium dioxide (UOX) core. These new experimental assemblies will have ceramic claddings and pellets which are able to operate at working temperature of Gas-Cooled Fast Reactor (GFR). This high temperature exceeds the safety limits of working conditions of the stainless steel MOX assemblies, consequently they have to be protected from the elevated temperature of experimental ceramic assemblies in the “mixed core”. In order to ensure thermal insulation between the two types of assemblies a thermal shield around the ceramic assemblies is planned. It consists of two parts: a thermal barrier which contains static helium and a cooling channel where helium flows bypassing the heated part of assembly. In this work we studied the effectiveness of the thermal insulation for different bypass flow rates in the cooling channel that can help to create the final design of experimental assemblies.

Methods

In the current work we created a 3D thermo-hydraulic model of the experimental assembly, containing the thermal shield and a part of fuel rod bundle. The final numerical model – which was used in this study as the basis of our calculations – was selected by sensitivity studies. We used realistic axial heat power distribution of fuel rods and the effect of convective and radiative heat transfer was also taken into account. Our primary aim was to determine the minimal bypass mass flow rate at which the thermal shield effectively insulates the experimental assembly from the neighbouring MOX assemblies. To ensure that the steel MOX assemblies are not heated by the ceramic ones we applied an adiabatic boundary condition on the outer surface of the assembly shroud. In this conservative case all the heat produced by the experimental assembly remains inside. If the surface temperature of the shroud of the experimental shield remains below the temperature of the neighbouring MOX assembly shrouds, then the experimental assembly would not heat the MOX assemblies. In our study we simplified this criterion using maximal temperature of modelled shroud surface and the average outlet temperature of the MOX assembly. The computational domain and its corresponding boundary conditions are shown in Figure 1 (left).

Results

The effect of the reduced bypass mass flow rate was studied by performing seven FLUENT code simulations from 100% to 1% relative flow rates. The results show that the maximum outlet temperature stays below the average outlet temperature of the MOX assembly [803 K] down to at least 5% relative bypass mass-flow rate as it can be seen in Figure 1 (right). Consequently, there is no positive heat transport towards the MOX assemblies and the thermal shield can work effectively when the relative bypass mass-flow rate is higher than 5%.

Related publication


Sensitivity Study of Decay Heat Removal Blower Pressure Loss in ALLEGRO Reactor

Gusztáv Mayer, Attila Guba

Objective

The nonrotating blower blades may bring about significant pressure loss in the decay heat removal (DHR) loop of ALLEGRO reactor, which hinders natural circulation. The higher is the pressure loss coefficient of the DHR blower blades, the worse core cooling is available during natural circulation in case of total station blackout (SBO) initiating event. On the other hand, a large core bypass develops if a DHR valve is opened inadvertently during normal operation and if the DHR blower is not rotating. In this case the lower DHR blower pressure loss is disadvantageous from core cooling point of view, because significant amount of coolant bypasses the core through the DHR loop in backward direction. This sensitivity study investigates how the pressure loss coefficient of the nonrotating blower influences the peak cladding temperature in the following two cases: 1.) SBO + LOCA (loss of coolant accident) and 2.) inadvertent DHR valve opening. Both cases may lead to insufficient core cooling in accident conditions, which threatens the integrity of the reactor core.

Methods

In this study the French CATHARE thermohydraulic code is used to assess the sensitivity of the DHR blower pressure loss coefficient in cases of total station blackout combined with LOCA, and inadvertent DHR valve opening. In the former case the break size and the number of operating nitrogen accumulators were varied, while in the latter case the inadvertent opening of 1, 2 and 3 valves were investigated.

Results

In Table 1 the calculated peak temperatures are depicted. Red colouring shows that the corresponding temperature criterion was exceeded.

<table>
<thead>
<tr>
<th>Initiating event</th>
<th>Break size (inch)</th>
<th>Number of nitrogen tanks</th>
<th>Peak Cladding Temperature [°C] (PCT)</th>
<th>PCT Criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBO+LOCA</td>
<td>1</td>
<td>1</td>
<td>815.19, 816.62, 829.79, 931.34, 1240.25</td>
<td>1300 °C</td>
</tr>
<tr>
<td>SBO+LOCA</td>
<td>1</td>
<td>2</td>
<td>809.13, 810.54, 823.40, 920.29, 1113.84</td>
<td>1300 °C</td>
</tr>
<tr>
<td>SBO+LOCA</td>
<td>1</td>
<td>3</td>
<td>808.08, 809.31, 822.16, 916.94, 1098.14</td>
<td>1300 °C</td>
</tr>
<tr>
<td>SBO+LOCA</td>
<td>2</td>
<td>1</td>
<td>912.76, 914.18, 927.21, 1044.08, 1312.82</td>
<td>1300 °C</td>
</tr>
<tr>
<td>SBO+LOCA</td>
<td>2</td>
<td>2</td>
<td>614.04, 612.48, 617.87, 646.54, 1062.32</td>
<td>1300 °C</td>
</tr>
<tr>
<td>SBO+LOCA</td>
<td>2</td>
<td>3</td>
<td>595.94, 595.94, 601.44, 818.26, 1300 °C</td>
<td></td>
</tr>
<tr>
<td>SBO+LOCA</td>
<td>3</td>
<td>1</td>
<td>1319.06, 1318.10, 1314.85, 1314.73, 1315.70</td>
<td>1300 °C</td>
</tr>
<tr>
<td>SBO+LOCA</td>
<td>3</td>
<td>2</td>
<td>892.74, 892.88, 900.18, 974.87, 1315.39</td>
<td>1300 °C</td>
</tr>
<tr>
<td>SBO+LOCA</td>
<td>3</td>
<td>3</td>
<td>755.87, 755.36, 757.16, 774.10, 1212.03</td>
<td>1300 °C</td>
</tr>
</tbody>
</table>

Pressure loss coefficient (backward direction) --------

<table>
<thead>
<tr>
<th>Initiating event</th>
<th>Peak Cladding Temperature [°C] (PCT)</th>
<th>PCT Criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 DHR valve opening</td>
<td>674.28, 672.19, 650.33, 618.91, 594.26</td>
<td>620 °C</td>
</tr>
<tr>
<td>2 DHR valves opening</td>
<td>792.31, 784.89, 743.96, 663.76, 609.82</td>
<td>850 °C</td>
</tr>
<tr>
<td>3 DHR valves opening</td>
<td>829.68, 920.67, 828.42, 711.37, 625.01</td>
<td>850 °C</td>
</tr>
</tbody>
</table>

The results showed that if the blower pressure loss coefficient is about 1.0 [1], then the SBO+LOCA event is manageable up to 3 inch break size using at least 2 nitrogen accumulators. On the other hand, (if the pressure loss value is small) in case of inadvertent opening of one or three DHR valves, the calculated PCT values exceeded the corresponding temperature limit.

Related publication

COMPLEMENTARY EXPERIMENTS FOR HIGH TEMPERATURE IRRADIATED SAMPLES

Levente Tatár

Objective
Innovative fission reactor types and fusion devices pose new requirements on the structural materials to be used. Existing materials may be adequate, but their fitness for purpose has to be proven experimentally. New tests have to be carried out for selected “candidate” materials. In the framework of the MATTER EU FP7 project, the most important candidate materials were P91 (ferritic steel) and 316LN (austenitic steel). MTA EK carried out high temperature irradiation experiments in the Bagira3 irradiation rig [1] for these materials. Due to shifting of interest from P91 to 316LN during the MATTER project, strength tests were carried out only on 316LN material. In the current work we complemented the experiments carried out in the framework of the MATTER project by new measurements.

Methods
The samples made of P91 and 316LN materials had been irradiated together in the Bagira3 irradiation rig. Irradiation conditions were described in [2]. For the 316LN material, in the framework of the MATTER project, Vickers hardness [3] measurements and instrumented Charpy measurements complying with EN 10 045 1 standard [4] had been done. These measurements were complemented by new hardness measurements on thermally aged specimens and instrumented Charpy measurements on unirradiated and thermally aged specimens.

In the framework of the MATTER project, specimens made of P91 steel were only prepared for testing. To complete the work, we performed three-point bending tests on the specimens and Master Curve analysis conforming to the ASTM E-1921 standard [5].

Results
For the 316LN material, the Vickers hardness has shown no real difference between irradiated, unirradiated and thermally aged specimens. The Charpy impact energy of the unirradiated and thermally aged specimens were above 300 J, so it could not be determined with our existing equipment, but results show a substantial reduction of the Charpy impact energy due to irradiation. For the P91 material, the results of Master Curve analysis are shown in Figure 1.

Remaining work
This project has been completed.

Related publications
III. NUCLEAR SECURITY AND DOSIMETRY
QUANTITATIVE IN-FIELD ANALYSIS OF UO₂ SAMPLES FOR DETERMINATION IMPURITIES USING PORTABLE LIBS SYSTEM

Éva Kovács-Széles, Csaba Tóbi

Objective

As part of the Hungarian Safeguards Support Programme (SP) to the International Atomic Energy Agency, a SP Task (number HUN A2282/17/TND-001) was started in 2017 with the title and topic of “Assessment of Capabilities of Portable LIBS for Impurity Content Determination in Uranium Bearing Materials”. This task supports extending the knowledge and providing of experimental data concerning the analytical capabilities of the promising emerging Laser Induced Breakdown Spectroscopy (LIBS) technology for use in the analysis of the purity of nuclear materials which can be used for identification of these materials and their origin for safeguards purposes. This project was the continuation of the task started in 2017.

Methods

For this task, the portable LIBScan25+ type Laser Induced Breakdown Spectrometer (LIBS) of MTA EK produced by Applied Photonics Ltd. was used. It contains a 50 mJ Nd:YAG laser and an SSD (solid-state drive) specific optical system, closed ablation cells and gas-flushing pressure system. A method for pelleting of UO₂ powder samples was also developed. ~750 kg/cm² pressure was the optimal condition to produce pellets with size of 5 mm diameter X 1 mm height, ~ 0.2 g weight. International Atomic Energy Agency rendered 3 reference materials (so-called work standards, measured by other laboratories) for MTA EK to use as calibration standards for the quantitative measurements.

Results

During this work, calibration curves for several elements were recorded during LIBS measurements. For this purpose, 3 reference materials were analysed in closed ablation chambers. One of the curves for Zn can be seen in Fig. 1. Several analytical performance parameters were also determined for the method, e.g. relative standard deviation: between 10-15% and detection limits: several 10 ppm, depending on the elements. Considering the solid-sample direct method with only 3 standards which has different matrix components, these parameters are satisfying.

![Figure 1: Calibration curve (Zn) for quantitative analysis by portable LIBS system](image)

Using the calibration standards, UO₂ materials available at MTA EK were analysed by LIBScan25+ system as real samples. As Table 1. shows, the measured concentration (determined by ICP-MS) agreed well with reference values.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample</th>
<th>ICP-MS reference value (ppm)</th>
<th>LIBS results (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>CMX4-3</td>
<td>643</td>
<td>775</td>
</tr>
<tr>
<td>Zn</td>
<td>CMX4-1</td>
<td>28,2</td>
<td>12,2</td>
</tr>
<tr>
<td>K</td>
<td>HU1-b</td>
<td>15,1</td>
<td>11,4</td>
</tr>
<tr>
<td>Mg</td>
<td>CMX4-3</td>
<td>44,6</td>
<td>44,5</td>
</tr>
</tbody>
</table>

Remaining work

Next steps of the work will be using real reference material with stable matrix and wide scale of elements, as well as concentrations, to refine the method. CRM-124 material will be transported from the Research Centre JRC Karlsruhe to MTA EK soon. CRM-124 contains 24 elements in 7 different concentrations. Elements are covering the real interest of the International Atomic Energy Agency.
Determining the Irradiation History of Spent Nuclear Fuel Using Gamma Spectrometry (2nd Year)

Péter Kirchknopf, András Kocsonya, István Almási

Objective

The Nuclear Security Department regularly measures the gamma spectra of spent fuel at Paks Nuclear Power Plant (NPP). Aside from the $^{134}$Cs and $^{137}$Cs isotopes, which give useful information on the burnup [1], other fission products (e.g. $^{106}$Ru, $^{144}$Ce and $^{154}$Eu) were also identified. The objective of this work was to develop a method based on the measured fission product activities that can be used to independently determine the irradiation history of spent fuel.

Methods

The principle of this technique lies in the production and depletion processes of fission products during in-operation and out-of-operation periods, so the activities of these isotopes depend on the irradiation history of the fuel assembly (e.g. no. of cycles, cycle length). By measuring these activities, some information could be deduced on the assembly history. The gamma measurements were carried out with a coaxial HPGe (High-Purity Germanium) detector. The theoretical activity values for a supposed irradiation history were calculated using the ORIGEN computer code. After this, comparisons were made between the measured and the calculated values. If they agree, the input parameters used in ORIGEN can be accepted as the assembly history. Otherwise modifications to the input need to be made for further calculations. The input parameters include the initial enrichment, the thermal power of the assembly and the duration of in- and out-of-operation times.

Results

For most nuclides, the difference between the experimental and theoretical activities was less than 25% (Fig. 1), except for $^{125}$Sb, which has a remarkably large discrepancy. The origin of these discrepancies is not yet clear. These results mean that the calculations with ORIGEN may not be accurate for the VVER-440 reactor type. Average correction factors were derived for the examined nuclides to keep the calculated activity ratios (with respect to $^{137}$Cs) in line with the measurements (Tab. 1).

![Figure 1: Deviation of the theoretical relative activities calculated with ORIGEN from the measured values](image)

Table 1: Multiplication factors to be used for correcting the activities calculated with ORIGEN

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Correction factor</th>
<th>1σ uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{95}$Nb</td>
<td>1.2501</td>
<td>2.8</td>
</tr>
<tr>
<td>$^{106}$Ru</td>
<td>1.1196</td>
<td>8.7</td>
</tr>
<tr>
<td>$^{110}$Ag</td>
<td>0.9605</td>
<td>12.6</td>
</tr>
<tr>
<td>$^{125}$Sb</td>
<td>0.5912</td>
<td>23.1</td>
</tr>
<tr>
<td>$^{134}$Cs</td>
<td>1.1333</td>
<td>10.2</td>
</tr>
<tr>
<td>$^{144}$Ce</td>
<td>1.3722</td>
<td>14.6</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>0.7795</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Activities were computed for several fuel histories with different cycle structures (Fig. 2a) and three thermal power levels (Fig. 2b). The large uncertainties caused by the correction factors, make it difficult to determine the exact assembly history.

![Figure 2: Relative activities for the $^{134}$Cs and $^{106}$Ru nuclide pair for different histories (a) and also for 80, 100 and 120% power levels (b). In the legend of (a), ‘1’ symbolizes one cycle of in-operation time and ‘n×0’ means n cycle of out-of-operation time](image)

Remaining work

The work could not be finished entirely as this was the 2nd year part of a 4-year project, the 3rd year part continues in 2019.

Related publication

IMPROVEMENTS ON MEASUREMENT TECHNIQUES FOR SOLID STATE NUCLEAR TRACK DETECTORS

Julianna Szabó, Andrea Strádi, József Pálfalvi, Attila Hirn, Tamás Pázmándi

Objective
This work was aimed to improve the evaluation methods for solid state nuclear track detectors used in various fields, especially in space dosimetry and radon measurements. Besides quickening the measurement also new types of investigations should be introduced as the following of track evolution through multiple sheets of a detector stack or through multiple etching steps.

Methods
The literature was browsed to find out what types of systems are used by groups involved in space dosimetry. Also the commercially available image analyser systems, usually optimized for radon (or neutron) measurements, were checked.

Results
It was found that for space dosimetry applications similar systems (optical microscope, digital camera) are used everywhere for imaging and usually home-made image analyser software tools are developed for measurements. The main difference compared to our system is the automatic stage movement and focus control, which enhances the rapidity of the evaluation. Most groups perform the track measurements offline after the automatic image acquisition. This method is quite fast, but as the system is just focused on the detector surface (left image in Fig. 1), measurements can be effectuated only in this plane. For the elliptical tracks, not numbered in Fig. 1, it is enough to determine only the minor and the major axis, these parameters can be measured in fully automatic mode.

However, in space there are born tracks for which, beside the minor and the major axis, the projected length and the depth where the track ends have also to be measured, see the track numbered 1 in Fig. 1. (These are usually the high atomic number and energy - HZE - particles and some short range secondaries, whose contribution to the dose equivalent can be significant). For the measurement of these parameters the focus has to be shifted to the appropriate plane (right image in Fig. 1). Our system is able to perform real time measurements on such tracks examining their three-dimensional geometry in manual mode. The development of automatic methods for these three-dimensional track measurements would be quite complicated, but the automatic stage movement control, which quickens the image acquisition, coming into production.

For radon measurements a fast, fully automatic system would be perfect. Our current system is good in automatic track recognition and with the automatic stage movement control it would be suitable also for these purposes.

Remaining work
The automatic stage movement control will enable the positioning with high precision. In addition, the examination of long range tracks through multiple sheets of a detector stack and the study of track development over multiple etching steps will also be easier. These are essential in investigations of primary and secondary radiations in space, see [1, 2].

Related publications

ANALYSIS OF THE MEASUREMENT RESULTS OF THE ENVIRONMENTAL RADIOLOGICAL MONITORING SYSTEM OF THE KFKI CAMPUS

Tamás Pázmándi, István Apáthy, Sándor Deme, Zsuzsa Endrödi, Dorottya Jakab, Andrea Strádi, László Tósaki, Orsolya Várady- Botvánszky

Objective

The main objective of this work was to analyse the active dose rate measurement results of the reconstructed gamma radiation monitoring network and compare them with those of passive dose measurements. In addition, integrated analysis of the environmental monitoring related to the occurrence of anthropogenic $^{106}$Ru in various environmental compartments was performed, which helped to validate the accuracy and representativeness of environmental measurements.

Methods

Part of the work was focused on the assessment of the gamma dose rate data gained during the operation of the reconstructed monitoring network. Correlation analysis was performed between the temporal variation of the measured gamma dose rate values at 17 critical points of the site and meteorological parameters, like precipitation.

The active gamma dose rate measurements were supplemented with passive dose measurements performed by TL dosimeters, which provided time integrated gamma dose rates following monthly readouts. PorTL and Pille dosimeters were installed at 13 points located around the primary nuclear facilities and radioactive material storages on the site. From these 13 points at 9 locations simultaneous measurements were performed with gamma dose rate meters and TL dosimeters, whereas at the remaining 4 locations parallel measurements were carried out with the two types of TL dosimeters. A database of about one year, which was obtained as the outcome of the simultaneous dose measurements, was evaluated.

Experimental characterization of the two types of TL dosimeter materials (Al$_2$O$_3$:C - PorTL; CaSO$_4$:Dy - Pille) was performed, their properties, as dose response, angular dependence and anomalous fading were investigated. In order to state whether the passive dosimeters are appropriate for environmental area monitoring, we also participated in an intercomparison. 20 Pille dosimeters have been sent to Germany, where some of them were exposed to terrestrial and secondary cosmic radiation for about 6 months, some were irradiated in a primary $^{137}$Cs photon field at two different angles, and a few were stored in an underground laboratory to determine the transport dose.

Anthropogenic $^{106}$Ru has been detected in the environment from late September to early October 2017 by several European environmental radiological monitoring networks - including the monitoring system in the KFKI Campus. $^{106}$Ru activity concentrations in environmental compartments (airborne particulates, deposition, terrestrial indicators) measured by the local monitoring system were evaluated. Potential dose consequences due to the $^{106}$Ru contamination were assessed, considering external exposure from cloudshine and groundshine and internal exposure via inhalation.

Results

The research resulted the following outcomes:

- The comparative analysis showed -12% average bias between the time integrated gamma dose rates of PorTL and Pille, while both passive dosimeters underestimated the ambient dose rate compared to the active dose rate meters.
- As the result of the experimental characterization, no significant differences were determined between the investigated properties (dose response, angular dependence and anomalous fading) of the TL materials.
- The results of the intercomparison for area photon dosimeters showed below 10% relative bias between the reported and target ambient dose equivalents, which can be considered as an acceptable difference in dosimetry.
- Residence time of the radioactive plume in the atmosphere and temporal variation of the $^{106}$Ru contamination was determined. Results were corrected with account taken of the relation between the sampling duration and the residence time of the radioactive plume, therefore directly comparable results were provided. There was a good agreement between the local results and the reported national and international values. According to the dose assessment, inhalation dose has been found as the main exposure pathway, which predominantly contributed to the total effective dose (150 nSv) in a short-term.
- Integrated analysis of deposition measurements and meteorological data was performed. The calculation indicated that wet deposition mechanism was the dominant contributor to the $^{106}$Ru deposition on the ground surface. In order to enable the separated sampling of wet and dry deposition, a special deposition sampling equipment was designed and manufactured. Separated sampling of wet and dry deposition will be started in 2019.

Remaining work

In order to identify the potential causes of the differences between the dose values, further investigation is required to determine the energy dependence and thermal fading properties of the used TL dosimeter materials.

Related publications


DEVELOPMENT OF MEASUREMENT METHODS FOR DETERMINING INTERNAL DOSE

Tamás Pázmáandi, Annamária Pántya, Dorottya Jakab, Gáborné Endrödi, Péter Zagyvai

Objective

Individual monitoring gives information needed to assess occupational and public exposure by measuring individual body activities, excretion activities or activity of inhaled air. For the great majority of incorporated radionuclides, the internal dose is estimated in two steps. In the first step the actual activity present in the body is determined by direct or indirect monitoring methods. By direct gamma spectrometric measurements activity in the whole or part of the human body can be determined (in vivo), while by indirect methods the radioactivity of physical and biological (in vitro) samples are assessed. In the second step the value of intake and the associated committed dose can be estimated on the basis of measured data considering necessary assumptions on exposure conditions (time and route of intake, chemical form etc.).

Methods

During this work, first of all we interpreted the new regulation (487/2015. (XII.30)) and new international recommendations (TECHREC and ICRP OIRs) and the renewed MSZ 62/7 which had been published in the recent years. Based on them, we reviewed the measurement practices applied for in vivo monitoring in MTA EK and then updated or developed measurement specifications for the determination of the internal exposure. The following methods were elaborated: whole body and part of body counting, thyroid measurement, measurement of gamma and beta emitter isotopes in urine, dose estimation. Calibration or quality control of the equipment has been carried out in accordance with the developed measurement procedures. In addition, we took part in several intercomparisons to verify the appropriateness of the methods.

Results

We presented technical steps for direct and indirect methods of monitoring individuals for occupational intakes of radionuclides. We described the steps needed to measure low- and high-energy photon emitters in the human body and to perform surface contamination check on individuals in order to distinguish between external and internal contamination. The procedure applies to all individuals undergoing in vivo monitoring of potential intakes of photon-emitting radionuclides into the human body at the Whole Body Counter (WBC) Laboratory. We fixed the steps required for equipment calibration, quality control and maintenance in the laboratory. They apply to calibration and regular maintenance of the NaI(Tl) and HPGe detectors used for low- and high-energy photon measurements to assure continuity of in-vivo individual monitoring service. Individual monitoring is extended to parts of body counting as well, namely to lung and thyroid. For this method, we also determined the optimal geometry and performed the necessary measurements, then the steps are summarized in a description. For each measurement the conditions of measurement shall be recorded (counting time, equipment and method used for measurement, limit of detection, name of operator, background count, and calibration). For indirect measurements we determined the measurement techniques and sample preparation method. The gamma emitter nuclides can be determined with HPGe detector in the low background chamber and the activity of soft beta emitter isotopes can be measured with liquid scintillator following an appropriate sample preparation. We have given the measurement instructions for both techniques. We describe the steps involved in the estimation of intakes and assessment of committed doses for workers with demonstrated amount of radionuclides in their bodies and/or excreta.

Remaining work

This project has been completed.

Related publications

Establishing the Methodology of Level 3 Probabilistic Safety Assessment

Tamás Pázmándi, Csilla Rudas, Péter Szántó

Objective

In the past decade there has been a growing interest worldwide in the development of a common, standardized Level 3 Probabilistic Safety Assessment (L3PSA) methodology. A couple of international meetings and workshops were organized by the International Atomic Energy Agency (IAEA) to facilitate sharing the knowledge and good practices of L3PSA, documents presenting the state-of-the-art L3PSA practices of the Nuclear Regulatory Commission (NRC) were published and an activity for conducting a comprehensive survey about L3PSA practices was launched by the Organisation for Economic Co-operation and Development (OECD). Currently, there is no Hungarian regulatory requirement for conducting L3PSA analysis. The aim of this work is to evaluate a L3PSA methodology for Hungarian conditions.

Methods

In this first phase of the work, the most important documents issued by the International Atomic Energy Agency (IAEA), the American Nuclear Authority (NRC) and the American Nuclear Society (ANS) were reviewed. The L3PSA practices in different countries based on the proceedings of the 2012 IAEA Technical Meeting in Vienna and the 2013 Regional Workshop in Warsaw as well as the results of the OECD survey were examined. Available codes which can be used to conduct off-site consequence analysis were evaluated based on the calculation models, the computational capabilities and the necessary input requirements.

Results

The review of the literature showed that there is no harmonized methodology in the field of L3PSA. The IAEA recommendation for conducting L3PSA analysis issued in 1996 presents a somewhat outdated methodology compared to current practices, in which the explanations and justifications for modelling considerations and omissions are not sufficiently detailed. The preliminary draft of a L3PSA standard issued by the ANS in 2017 defines requirements for the probabilistic analysis of atmospheric radioactive releases, describes the methodology for each calculation step and the appropriate documentation procedures. The requirements are flexible, the modelling decisions are not fixed but can be chosen based on the application of the calculation, thus the standard can widely be used.

The practices of countries that perform L3PSA or conduct research in the field are summarized in Table 1. In Korea and the Netherlands, there are regulatory requirements for L3PSA analysis when applying for a license for establishing, constructing, commissioning, operating or decommissioning nuclear installations. Despite not being legally required to do so, Japan and the USA perform L3PSA calculations to verify the fulfillment of quantitative safety objectives, to improve emergency preparedness and response, to optimize severe accident management strategies and to conduct environmental impact assessments. In Finland and Sweden significant research is underway to assess L3PSA practices, to standardize the calculation methodology, to develop regulatory guidelines and to launch pilot studies. The MACCS software is widely used for L3PSA calculations (in Korea, the USA, the Netherlands and Finland), however, this code is not easily applicable for methods and modelling considerations which differ from the US practices. As a result, some countries are developing or planning to develop their own L3PSA software (OSCAAR - Japan, NUDOS – the Netherlands, LENA – Sweden, ARANO – Finland). Two deterministic codes (COSYMA and RODOS) can be used for limited probabilistic assessments, as they contain statistical analysis tools for considering different weather scenarios or countermeasure strategies.

Table 1: Summary of the international practices of L3PSA

<table>
<thead>
<tr>
<th>Country</th>
<th>Regulation</th>
<th>L3PSA calculation</th>
<th>Objective</th>
<th>Software</th>
<th>L3PSA for NNPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Korea</td>
<td>yes</td>
<td>yes</td>
<td>Risk Criteria</td>
<td>MACCS</td>
<td>n.a.</td>
</tr>
<tr>
<td>The Netherlands</td>
<td>yes</td>
<td>yes</td>
<td>Risk Criteria</td>
<td>COSYMA</td>
<td>Borssele</td>
</tr>
<tr>
<td>USA</td>
<td>no</td>
<td>yes</td>
<td>Risk Criteria, Environmental Impact Assessment</td>
<td>MACCS</td>
<td>Surry, Peach Bottom, Zion, Sequoyah, Grand Gulf</td>
</tr>
<tr>
<td>Japan</td>
<td>no</td>
<td>yes</td>
<td>Risk Criteria, Emergency Response</td>
<td>OSCAAR</td>
<td>n.a.</td>
</tr>
<tr>
<td>Finland</td>
<td>no</td>
<td>yes</td>
<td>Research</td>
<td>ARANO</td>
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</tr>
<tr>
<td>Sweden</td>
<td>no</td>
<td>interest</td>
<td>Research</td>
<td>LENA</td>
<td>no</td>
</tr>
</tbody>
</table>
**Remaining work**

In the next phase of the work, the Hungarian legal environment and the possibility of introducing L3PSA regulatory criteria will be explored. The resources necessary for conducting L3PSA will be investigated.

**Related publications**


STUDY OF THE RADIATION FIELD IN THE UPPER ATMOSPHERE

Balázs Zábori, Attila Hirn

Objective
The present research focuses on determining the characteristics of the radiation field in the near-Earth region based on measurements performed in space experiments and then, based on these results, aims at giving a detailed description of the radiation field and its dosimetry.

Methods
Measurements had been performed and analysed in the preceding years on board stratospheric balloons and on a sounding rocket. To extend the region of interest around the Earth, a space radiation detector (ESEO-TRITEL) had been developed, manufactured and tested to be operated on board the European Student Earth Orbiter (ESEO) satellite in the frame of a European Space Agency education program. Acceptance tests of the 3D silicon detector ESEO-TRITEL were performed first at payload level. These were followed by integration tests on the payload connected to the ESEO flatsat and by mechanical fit checks to the satellite structure. The final environmental acceptance tests were performed after integration of the satellite, including vibration, thermal-vacuum, and electromagnetic compatibility (EMC) tests.

Results
The integration test campaign of the ESEO-TRITEL protoflight model was successfully completed. The payload passed the final environmental tests and it was ready to be launched into space at the time of the report was written.

Related publications

MODELLING THE TRANSPORT OF RADIONUCLIDES IN SURFACE WATER: PART 4

Barbara Brockhauser, Sándor Deme, Tamás Pázmándi, Csilla Rudas, Péter Szántó

Objective

The objective of the research of modelling the transport of radionuclides in surface water is the development of a dynamic transport model that estimates the environmental radiation resulting from an accidental radioactive emission from the Paks nuclear power plant (NPP). In the last phase of the 4-year project, a software and documentation were developed based on the established aquatic transport model that can determine the consequences of a liquid release from Paks NPP and calculate the dose for different aquatic pathways.

Methods

The developed aquatic transport model uses local and site specific geological and hydrological data including the local shape of the river’s cross-section, the water level dependent flow rate, the flow velocity and also the local sediment data. Sensitivity analyses were conducted to determine the most important input parameters of the program.

Results

According to the analyses, one of the most important parameters is the river water level as it changes frequently, and has a huge influence on other hydrological parameters. Figure 1 shows the daily change of the water level in 2017 for the Danube at Paks. Analysing the average monthly data for the last 10 years, it can be seen that the highest river stages occur late spring and early summer. The lowest water levels were measured during autumn and winter-time.

![Figure 1: The daily change of the water level at Paks during 2017](image1)

Further calculations were made with the program to determine a connection between the activity concentration in the water and the water level [1]. In the calculation, the released activity was considered to be 1E+16 Bq I-131, and the correlation between the activity concentration and the water level can be seen in Figure 2. It is conspicuous that increase in the water level decreases the activity concentration at shore side. Additional study was conducted to see the behaviour of the lateral mixing of the activity concentration depending on the season. Measurement results suggested that the cross-sectional distributions of the activity concentration are almost the same in the autumn and winter (AW) and also in the spring and summer (SS) time, therefore these seasons can be considered together. The lateral distribution of the activity concentration for autumn-winter and the spring-summer time is shown in Figure 3.

![Figure 2: Connection between the calculated activity concentration (line) and the water level (columns)](image2)

![Figure 3: The lateral distribution of the activity concentration for autumn-winter and spring-summer time](image3)

The SS time has higher water level, therefore the lateral mixing is better, so the activity concentration at shore side is 1.5 times lower than during AW time. Most of the activity concentration occur in the first 100 m for both cases.

Remaining work

This project has been completed.

Related publication

DEVELOPMENT OF THE SYSTEM FOR EVALUATING THE RADIATION SITUATION – DEVELOPING THE DATABASE

Tamás Pázmándi, Péter Szántó

Objective

The primary objective of the four-years-long work is to develop a system for the evaluation of the radiation situation in Hungary. The system consists of meteorological and radiological database. The input data for the database are provided by the members of the Hungarian radiological measurement network. The data in the system will be used to provide information on the radiation situation in Hungary. In emergency situations, the system will also be used to estimate the possible sources of the release.

Methods

The state of the current Hungarian regulatory framework for monitoring systems is fragmented. There are two monitoring systems in Hungary, OKSER (National Environmental Radiation Protection Control System) and OSJER (National Radiation Observation and Control System). They are being overseen by different organizations and institutions. The systems consist of their own stations established by the operating organization, most of stations can be part of both systems. In the already established, long-lasting and satisfactorily operating Hungarian practice, the monitoring of accidental (emergency) and normal (planned) radiation situations is regulated separately and is mostly performed by the same systems but according to different protocols. In order to implement the changes in the regulation, we have designed the database structure for the operation of the data analysis and representation system. The purpose of creating the database is to store the radiological and meteorological data received from the monitoring systems. The requirements towards the database cover the following points:

− content requirements: needs to contain all data from radiological monitoring systems, needs to be able to handle any measurement data generated during a radiological emergency, and needs to be ready to store the results of model calculations for atmospheric dispersion, like the SINAC decision support system used in Hungarian Atomic Energy Authority Centre for Emergency Response, Training and Analysis (OAH CERTA),
− structural requirements: needs to be able to easily filter, render searchable for future representations and analyses, and needs to be easily expandable when the monitoring system develops and changes,
− system requirements: SQL-based IBM DB2 database is recommended to manage the database,
− format and access requirements: needs to be compatible with the requirements of the International Radiological Information Exchange (IRIX) and European Radiological Data Exchange Platform (EURDEP) formats.

Results

The structure of the system responsible for storing the data is shown in Figure 1. In the current part of the work, the middle element, the database structure was developed.

![Figure 1: The structure of the system](image)

It has been found that the assessment of the radiation situation in different cases (in normal, accidental and existing radiation situations) should be made by considering the different aspects derived from the given irradiation situation. In any case, the assessment of the situation is influenced by the limited capacity of the measurements. Showing measurement data on graphs or maps, supplementing them with the results of model calculations, occasionally helps the assessment of the situation and the work of the decision makers.

Remaining work

In the following stages of this work, details of the system will be evaluated and the introduction of the developed system will be performed.
SPACE DOSIMETRY FOR HUMAN SPACEFLIGHT AND BIOSATELLITE RESEARCH

Attila Hirn, István Apáthy, Antal Csőke, Sándor Deme, András Gerecs, Eszter Pálfalvi, József K. Pálfalvi, Tamás Pázmándi, Andrea Strádi, Julianna Szabó, Balázs Zábori

Objective

Space dosimetry and space weather activities of the MTA EK research centre are concentrated in the Space Dosimetry Research Group. Several dosimeter systems developed by the group operate on board the International Space Station (ISS) with the aim of providing information on the dose distribution at different locations with different shielding conditions and also personal dosimetry. Maintenance, scientific and technical support during operation and upgrade of these systems are key tasks of the group. In parallel, different types of silicon detector telescope systems have been and are being developed for satellites in low Earth orbit. The activities reported in the present paper have been realized in cooperation with the Institute of Biomedical Problems (IBMP), Russian Academy of Sciences and S. P. Korolev Rocket and Space Corporation Energia.

Methods

The Pille space-qualified thermoluminescent (TL) dosimeter system, developed in our institute, provides accurate and high resolution absorbed dose data. In 2018, a new Pille TL Reader (No. 20) was sent to the ISS to replace the unit No. 16 that already has been operated on board without any degradation or malfunction since 2003, but the warranty of which expired. Pille is operated as part of the service dosimetry system of the Russian Segment. It comprises a set of dosimeters and an on-board reader. For on-board stability analysis, from time to time, all dosimeters are placed on panel No. 327 for two weeks, and the quasi-homogeneous radiation field at that position is used as natural calibration radiation source. The correction factors for the individual dosimeters are then calculated from the results of the sensitivity measurements. In the frame of the commissioning of the new Pille Reader and the dosimeters delivered, first all new Pille dosimeters were read out with Pille Reader No. 16. This was followed by on-board cross-calibration campaigns, with each new dosimeter being paired with an old one and each pair being placed at different locations for 25 days and 36 days. Read-outs were performed by both Pille Readers.

Bion-M2 is a returnable biological satellite programme led by IBMP. The objective is to study zero-gravity and space radiation impacts on living organisms at about 800 km above the Earth's surface. TRITEL-B is one of the scientific payloads on the returnable capsule, to be developed in MTA EK, with the aim of supporting biological experiments with dosimetry data. Radiation transport calculations were performed with the Space Environment Information System (SPENVIS) online tool to support development of the detector concept based also on the three-dimensional silicon detector system, TRITEL.

Results

In year 2018, approx. 6000 measurements were performed with the Pille system. The data obtained were evaluated. In the first read-out of the new Pille dosimeters, following an exposition of 122 days (85 days on ground, 37 days in space), the maximum deviation from the average was 4%, significantly smaller than the maximal deviation of ±10% allowed by the international standards for TL detectors. In the cross-calibration campaigns, the deviation of the average for all Pille dosimeters were within ±10%, except A0301 and A0311. These two dosimeters have been used for automatic read-out for years, their slight degradation was known. The accuracy of all of the new Pille dosimeters (No. A0151 – A0155) and the Pille Reader No. 20 met the specifications; their regular use on ISS is allowed.

By means of reconfiguration of the three silicon detector pairs in TRITEL to form a one-dimensional triple telescope with aluminium absorbers in-between the detector pairs, and integration of the passive detector package containing solid state nuclear track etch detectors and thermoluminescent detectors into the instrument, a measuring package capable of providing depth-dose and depth LET (Linear Energy Transfer) information for the biological experiments was proposed. The preliminary dose calculations have shown that the average dose rates expected at different depths differ only about 20% for the two possible inclinations of the Bion-M2 orbit. The highest absorbed dose rate is expected just behind the wall of the capsule (~1 mGy/h). The dose rates at the largest depth is ~0.5 mGy/h.

Remaining work

Evaluation and interpretation of the measurement data produced by the Pille and TRITEL dosimeter systems on board ISS, as well as maintenance of these instruments will be pursued. Definition and development of the preliminary design of the TRITEL-B experiment for the BION-M2 biosatellite will be continued.

Related publications

TRITEL Instrument On Board the ESEO Satellite

Balázs Zábori, Attila Hirn, András Gerecs, István Apáthy, Boglárka Erdős, Anna Baranyai

Objective

The development of the European Student Earth Orbiter (ESEO) was announced in the year 2008 by the European Space Agency (ESA) for students interested in space activities. ESEO is an educational hand on project of the ESA Education Office, carried out as part of the ESA Academy programmes. It is stated in the ESEO mission objectives: “measure the ionizing radiation environment in orbit”. The ESEO-TRITEL payload will fulfil this objective during the mission of the satellite. The MTA Centre for Energy Research (MTA EK) is responsible to support, coordinate and provide professional background for the ESEO-TRITEL student team which is responsible for the ESEO-TRITEL payload development activities. The activity of the University students’ teams was coordinated by SITAE L S.p.A. (Italy), System Prime and Integrator of the whole spacecraft platform.

Methods

In order to study the cosmic radiation field in orbit for dosimetric purposes, the development of a three dimensional silicon detector telescope (TRITEL) with almost uniform sensitivity got underway in the former KFKI Atomic Energy Research Institute (AEKI, now part of MTA Centre for Energy Research) in the last decade. The instrument comprising three mutually orthogonal, fully depleted PIPS (Passivated Implanted Planar Silicon) detector pairs are designed to measure the energy deposition of charged particles. The main design goal in the frame of the ESEO mission is to design, develop, manufacture and verify through intensive test campaign a new, satellite version of the TRITEL instrument.

Results

Following the authorisation ESA to manufacture the ESEO-TRITEL flight model an intensive acceptance test campaign was carried out covering specific manufacturing related inspections, functional tests, calibration activities, vibration tests, thermal-vacuum (T-VAC) tests, electromagnetic compatibility (EMC) tests. The ESEO-TRITEL team was responsible to carry out the extensive test programme in the light of the ECSS (European Cooperation for Space Standardization) standards. Most of the tests were carried out in the internal facilities of MTA EK, only some specific calibration activities, the vibration and EMC tests were performed in external locations. Finally, the flight model was accepted by ESA and it was delivered to Italy for higher level satellite integration and test activities. After the ESEO satellite integration it was shipped to the technology test centre of ESA for final satellite level acceptance testing, including vibration, T-VAC and EMC tests. It was verified that the satellite and the ESEO-TRITEL instrument are ready for launch (Fig. 1). The ESEO satellite was launched on 03.12.2018. from US (United States) Vandenberg Air Force Base on board a Falcon-9 rocket operated by SpaceX (the mission name was SpaceX’s SSO-A mission). The ESEO satellite activated itself just after separation from the launch carrier and started transmitting beacon signals, which were received by the ground control of the mission. The ESEO-TRITEL project is realized in the frame of PECS contract No. 4000112065 and the ESA PRODEX contract No. 4000124167.

Related publication

Dose Distribution Inside the International Space Station-3D/DOSIS 3D

Julianna Szabó, Andrea Strádi, Attila Hirn, Balázs Zábori, József K. Pálfalvi

Objective

The aim of the DOSIS 3D project is the measurement of the radiation environment inside the International Space Station (ISS). The project is organized by the European Space Agency (ESA) under the leadership of the German Aerospace Centre (DLR), with the participation of research groups from all around the world. MTA Centre for Energy Research (MTA EK) is responsible for the provision of passive radiation detectors for the measurement of the absorbed dose, Linear Energy Transfer (LET) spectra and dose equivalent. These activities are funded in the frame of the ESA PRODEX Experiment Arrangement No. 4000124183. DOSIS 3D had been started in the year 2012 and after several extensions it was prolonged till the remaining lifetime of the ISS. It consists of approximately half-year long exposure cycles (phases). The current report reflects the contribution of MTA EK until the end of 2018, with emphasis on the most recent phase No. 12.

Methods

Thermoluminescent detectors (TLDs) and solid state nuclear track detectors (SSNTDs) are applied by the MTA EK Space Dosimetry Research Group to investigate the dose contribution of the low (<10 keV/µm) and the high (>10 keV/µm) LET cosmic radiation. The plastic detector boxes contain two SSNTD sheets and six or eight TLD pellets (half of them is made of 6Li enriched MTS-6 material, the other half is 7Li enriched MTS-7). In each phase there are 10 single boxes and a set of 3 boxes (arranged in the 3 directions of space) installed inside the European Columbus module. For a better understanding of the properties of the applied radiation detector systems, an extensive ground intercalibration program is applied as an indispensable part of the work with contributions from all participating investigators.

Results

As in the previous phases, the doses measured in phase 12 by the MTS-6 pellets were somewhat higher than the MTS-7 signals, indicating the presence of secondary neutrons, see Fig. 1. Fig. 2. presents the dosimetric quantities measured by SSNTDs. The tendency observed in case of the different locations with different shielding conditions is similar for the high and for the low LET radiation: the highest doses were measured in Boxes 2, 6 and 7, as usually.

![Figure 1: Absorbed dose rates obtained by TLDs, phase 12](image1)

![Figure 2: Absorbed dose and dose equivalent rates obtained by SSNTDs, phase 12](image2)

The doses measured by the MTS-7 pellets were appropriately combined with the SSNTD results to obtain the total absorbed dose and dose equivalent values. Their ratios gave quality factors between 2.4 and 2.9.

Remaining work

According to the current plan the project continues till 2024. The interpretation of the vast amount of data is in progress. An interactive database is going to be built, serving the scientific community and holding essential information for the application of radiation protection standards for manned spaceflight and for any radiation susceptible experiment in space.

Related publications


Objective

The research on space weather and its effects will be more and more important in the near future, as a continuous increase in human presence is in progress in the Near-Earth region and the technology dependency of the human civilization has become higher than ever mainly in the fields of energy and telecommunication systems. To study space weather and to protect our technology, as a first step, it is necessary to develop and establish an advanced monitoring system to provide scientific data about the space radiation intensity and the status of the magnetosphere in order to achieve the possibility for a reliable forecast database. Thus development of new space weather related instrument technologies got underway at the Centre for Energy Research, Hungarian Academy of Sciences (MTA EK), based on silicon detector technology including magnetic field measurement capabilities. By having a compact design realized following CubeSat/SmallSat standards, the monitoring of space radiation and magnetic field environment will be possible with sufficient statistics in the Near-Earth region on board a fleet of CubeSats/SmallSats as a part of ESA’s (European Space Agency) hosted payload mission concept. Additionally, the developed instrument technology can provide a low-cost alternative for supporting radiation damage estimations commercially for future satellite missions as well. All these activities are realised in international cooperation.

Methods

In the frame of the Space Weather Service Network (SWE) segment of the ESA Space Situational Awareness (SSA) programme ESA requested an operational space weather prediction system with appropriate databases originating from near-real time service provider instruments/payloads in order to offer space weather related services. Since the space weather environment of the Earth is highly influenced by several physical parameters (magnetic field variability, cosmic ray intensity, solar activity, atmosphere, etc.) and mainly due to the complexity of the magnetosphere, a very good spatial and time resolution is required in space weather monitoring. To fulfil this goal ESA defined the Distributed Space Weather Sensor System (D3S) concept utilizing hosted primary and secondary payloads (instruments) for operational space weather monitoring on board as many platforms as possible.

In the framework of the ESA General Support Technology Programme (GSTP) MTA EK has initiated the RADCUBE In-Orbit Demonstration (IOD) mission including the development of a new instrument, called RadMag. The major goal of the RADCUBE mission is to demonstrate the space weather service capabilities of a CubeSat mission to the ESA SSA SWE programme segment. However, the development of the RadMag instrument is very much restricted by the technical constraints of a typical CubeSat mission, thus, in parallel, MTA EK initiated a similar development in collaboration with ESA experts, called D3S-RadMag instrument concept.

The major goal of this concept is to provide a market product combining the radiation and magnetic field measurement capabilities into one payload to be directly applicable within the D3S hosted payload concept of ESA. The conceptual approach shall take into account modularity as design driver in order to make possible to accommodate it on different platforms as a hosted payload. Modularity means that a general, core electrical system (data acquisition and control, power supply and communication) will be designed which can handle the sensor systems attached. The following can be added to the instrument core system in accordance with the given hosting mission/platform possibilities: different radiation measurement telescopes with signal processing, radiation hardness assurance (RHA) related monitoring capabilities (e.g., RHA boards, Total Ionizing Dose (TID) monitoring boards), magnetometer sensor(s) with signal processing (internal and external 3-axis magnetometer sensors). This concept provides a highly variable instrument, which can be fitted to the given hosted mission regarding the sensor system selection (sensor selection will be based on the expected space weather environment and mission constraints, like available volume, mass, power, etc.). As a significant optional component the instrument concept shall feature the capability of providing radiation hardness assurance and monitoring dosimetric quantities, like TID, which can be offer a commercial service for the platform system providers. This will make the instrument favourable for the possible platform providers and means higher chance to have it on board as a hosted payload as many times as needed. At the moment, there is no such complex instrument available on the market or under development as hosted payload candidate which can fulfill all of the above given needs, has the capability of variable sensor system for the given hosted mission and combines the space radiation and magnetic field monitoring capabilities.

Results

The RadMag CubeSat instrument development reached its final design phase by closing the design of the Engineering Qualification Model (EQM). Prior to the design closure an Engineering Model (EM) was designed and manufactured for performance testing in order to verify the design concept. The instrument EM was tested in-house, at MTA EK, by using radiation sources. In addition, a test campaign was carried out at the Paul Scherrer Institute (PSI) in Switzerland with monoenergetic electron and proton beams. The test results verified that the instrument performance is in-line with the previously performed detailed radiation transport analysis.
In the frame of the D3S-RadMag instrument development, the detailed instrument requirements list was elaborated following ESA’s standards and the general requirements of the D3S mission concept. The requirement list will be used during the detailed instrument design. In parallel the radiation telescope concept was iterated based on detailed radiation transport simulation activities (see Fig. 2) with the involvement of ESA experts in order to define the optimal measurement technique from performance, technological and cost point of view.

**Remaining work**

In case of the RadMag instrument development the EQM model will be manufactured in 2019 followed by an intensive qualification test campaign in the frame of the RADCUBE mission. It will be pursued by the Flight Model (FM) manufacturing and acceptance testing. The launch of the satellite is expected in 2020 with a minimum of 6 months in-orbit operation for the RadMag instrument.

In case of the D3S-RadMag instrument development the design of the EM model shall be finalized by finishing the radiation transport simulations. The EM model shall be manufactured and tested in relevant facilities. In parallel, the first IOD flight opportunity for the D3S-RadMag instrument will be identified together with ESA and the related development roadmap shall be investigated.

**Related publication**

PREPARATION FOR EXPERIMENTAL STUDIES OF RADIATION RESPONSE AT THE CELLULAR LEVEL

Balázs Madas, Emese Drozsdik

Objective

In the past years, mathematical models of radiation response have been elaborated with potential implications on the fundamental principles of radiation protection. Experimental validation of our model predictions is highly desirable. Therefore, the objective of the present study was to get acquainted with experimental techniques in basic radiation biology which can later be applied for validation of our theoretical results.

Methods

We strengthened our existing national and international collaborations with experimental groups and established new ones. In these collaborations, we build on our skills in dosimetry and mathematical modelling, while we aim to be involved and to gain experience in experimental radiation biology. Specific research goals were to take the next steps in i) the estimation of the relative biological effectiveness (RBE) of cold neutrons for the induction of chromosome aberrations and micronuclei in blood lymphocytes, ii) the preparation of experiments on cell viability as the function of absorbed dose with biosensors, iii) the determination of the distribution of deoxyribonucleic acid (DNA) double strand breaks (DSBs) upon exposure to alpha-particles emitted by radium-223 and its progeny, and iv) the quantification of the radiation response of in vitro reconstructed bronchial epithelial tissue upon microbeam exposure with alpha-particles.

Results

Exposure of lymphocytes to cold neutrons was planned for the mid-November cycle of the reactor. Ratio of absorbed dose from gamma-radiation and cold neutrons was measured in the previous cycle by thermoluminescent dosimeters. The total absorbed dose was surprisingly high with much higher dose contribution from γ-photons than expected, contradicting to theoretical calculations.

A first draft of experimental design has been prepared for cell viability measurements with biosensors involving the nanobiosensorics and space dosimetry group of our Research Centre. Survival curves will be determined by a methodology completely new in the field. The experimental setup can be applied to test our model predictions on low dose hyper-radiosensitivity and on induced radio-resistance relating the phenomena to mutation induction [1].

Hit and dose distributions in cancer cells exposed to alpha-particles emitted by radium-223 and its progeny have been determined by Monte-Carlo methods [2]. Results revealed that earlier measurements on cell size were inappropriate. New experiments were planned based on our computations. Simulations were used to estimate the contribution of alpha-particles to DNA damage in a mixed field exposure scenario [3].

Earlier, increased proliferation rate has been observed in in vitro reconstructed epithelium after high dose exposure with alpha-particles emitted by americium-241. The experiment was repeated this year with smaller doses precisely targeted with an alpha-particle microbeam. The motivation of these studies was to test our predictions on the induction of progenitor cell hyperplasia in the bronchial epithelium upon chronic exposure to radon progeny [4,5].

Remaining work

Monte-Carlo simulations have to be performed for more precise estimation of absorbed dose in blood exposed to cold neutrons. In order to perform viability experiments with biosensors, funding should be secured. The manuscript on the cellular responses upon exposure to alpha-particles emitted by radium-223 and its progeny has to be prepared. Evaluation of tissue response upon microbeam exposure is on-going. A manuscript on the results is also expected to be submitted next year.

Related publications

RESEARCH ON THE BIOPHYSICAL EFFECTS OF LOW DOSES OF IONISING RADIATION

Árpád Farkas, Balázs G. Madas, Péter Füri, Emese Drozsdik, Ágnes Jókay, Tamás Pázmándi, Imre Balásházy

Objective

The research objectives for the year 2018 were:

1. use of the Stochastic Lung Model for the quantification of cellular activity- and dose-distributions due to deposition and clearance of radon progenies in the airways at radiation exposure conditions characteristic of homes,
2. numerical modelling of low dose hypersensitivity using an analysis of the possibility to explain the phenomenon by the principle of the minimisation of mutations,
3. combination of the Lawrence Livermore National Laboratory (LLNL) voxel phantom and the Stochastic Lung Model (SLM) for the calibration of the whole body counter measurements.

Methods

1. A numerical model for the quantification of deposition and clearance of the inhaled radon daughter products in airways has been developed and used. Applying the model absorbed doses in the nuclei of radiosensitive epithelial cells due to alpha-decay of the inhaled short-lived radon progenies were calculated.
2. A mathematical model has been developed in which the cells are supposed to die or survive depending on which of the two events results in a lower mutation number within the cell population.
3. The lung surfaces were reconstructed based on medical images provided by the Karlsruhe Institute of Technology. The Stochastic Lung Model was further developed to fill the airspace delimited by these surfaces with the branching airways of the human tracheobronchial tree.

Results

1. Based on the simulation results, the radiation burden of the inhaled radon decay products is spatially inhomogeneous within the bronchial airways. This suggests that the characterization of radiation burden at the regional level (e.g. upper airways, bronchial airways, acinar airways) is not sufficient for the assessment of radiation risks. It was demonstrated that quantification of the exact radiation burden due to the inhaled $^{214}$Po is not possible without airway generation level modelling of mucociliary clearance.
2. The simulation results confirmed the theory that minimisation of mutations at any dose results in local minima of the survival curve. If a certain dose causes more mutations, then the minima are lower, which explains why hypersensitivity was observed predominantly in the case of cancerous cells.
3. The LLNL-SLM model described in the Methods section has been successfully constructed and tested. The spatial distribution of the inhaled radionuclides deposited in the model airways was simulated. The distribution of the activity due to the deposited isotopes was also computed.

Remaining work

The results of the activity distribution in the voxel phantom will serve as inputs for the model, which estimates the amount of gamma radiation at the location of the detector of the whole body counter.

Related publications

Rapid Separation of Actinides from Human Urine, Soil and Sediment Matrices by Extraction Chromatography

Márton Zagyvai, Nóra Vajda (Radanal Ltd.), László Szentmiklósi

**Methods**

Diglycolamide (DGA)® is a commercially available resin that contains N,N,N’,N’-tetra-n-octyldiglycolamine on an inert support. Am, U, Pu and Th are separated by extraction chromatography using DGA resin. A previously applied method [1] was simplified by omitting the digestion and preconcentration steps before the step of separation on DGA resin. 100 mL of water and 100 mL urine samples acidified with 50 mL of HCl to 4M were loaded on to a 0.5 g DGA column. Alpha-sources of various actinides were prepared by co-precipitation with NdF₃ from solutions following separation. Activity measurements were performed with a Si α-detector. We started developing this method for samples taken from a nuclear reactor coolant as well as for those from the environment, e.g., for soil and sediment samples. We used NaOH fusion on soil and sediment samples to get rid of silicate that badly affected the separation process.

**Results**

This year we investigated further the effect of urea (Table 1.) [2] as a relevant constituent of human urine. We made model experiments with distilled water assuming that urea has an effect on the retention of americium and thorium, but the subsequent results did not verify this theory. We studied the effect of the skipping the step of urine destruction with NaOH on the retention of the four actinides. We found that the lack of destruction has a notable effect on the retention of thorium and uranium (Pi50 experiment).

<table>
<thead>
<tr>
<th>No. of experiment</th>
<th>Recovery (%)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th-230</td>
<td>U-233</td>
<td>Pu-239</td>
</tr>
<tr>
<td>Pi43</td>
<td>42</td>
<td>89</td>
</tr>
<tr>
<td>Pi44</td>
<td>46</td>
<td>105</td>
</tr>
<tr>
<td>Pi45</td>
<td>82</td>
<td>-</td>
</tr>
<tr>
<td>Pi46</td>
<td>33</td>
<td>81</td>
</tr>
<tr>
<td>Pi50/1</td>
<td>29</td>
<td>18</td>
</tr>
<tr>
<td>Pi50/2</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Pi50/1+Pi50/2</td>
<td>49</td>
<td>20</td>
</tr>
</tbody>
</table>

We compared the method we developed with a previous method [3] which included destruction and separation on TRU resin. We used urine samples from contaminated persons (Table 2).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Recovery (%)</th>
<th>Am-241 activity concentration (mBq/L)</th>
<th>Uncertainty (%)</th>
<th>LD</th>
<th>Recovery (%)</th>
<th>Am-241 activity concentration (mBq/L)</th>
<th>Uncertainty (%)</th>
<th>LD</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>91</td>
<td>LD</td>
<td>-</td>
<td>1,8</td>
<td>64</td>
<td>LD</td>
<td>-</td>
<td>0,44</td>
</tr>
<tr>
<td>D</td>
<td>81</td>
<td>3,22</td>
<td>23</td>
<td>1,3</td>
<td>86</td>
<td>5,63</td>
<td>28</td>
<td>0,38</td>
</tr>
<tr>
<td>K</td>
<td>83</td>
<td>6,14</td>
<td>15</td>
<td>1,6</td>
<td>73</td>
<td>19,53</td>
<td>23</td>
<td>0,64</td>
</tr>
</tbody>
</table>

The lower recoveries of the DGA procedure are caused by the omission of the destruction step. We think other reasons are responsible for the other differences in the results. We will implement further experiments. We have started applying the method to soil and sediment samples with NaOH fusion.
Table 3: Results of fusioned soil and sediment samples

<table>
<thead>
<tr>
<th>Sample code</th>
<th>326a Activity (Bq)</th>
<th>326a Bq/kg</th>
<th>326a Recovery (%)</th>
<th>326b Activity (Bq)</th>
<th>326b Bq/kg</th>
<th>326b Recovery (%)</th>
<th>375 Activity (Bq)</th>
<th>375 Bq/kg</th>
<th>375 Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am-241</td>
<td>0,0080</td>
<td>1,59</td>
<td>84</td>
<td>0,0055</td>
<td>1,10</td>
<td>69</td>
<td>0,001</td>
<td>0,17</td>
<td>90</td>
</tr>
<tr>
<td>Pu-238</td>
<td>0,0033</td>
<td>0,65</td>
<td>66</td>
<td>0,0045</td>
<td>0,89</td>
<td>45</td>
<td>LD</td>
<td>-</td>
<td>35</td>
</tr>
<tr>
<td>Pu-239,240</td>
<td>0,0040</td>
<td>0,80</td>
<td>66</td>
<td>0,0042</td>
<td>0,84</td>
<td>45</td>
<td>0,004</td>
<td>0,7</td>
<td>35</td>
</tr>
<tr>
<td>U-234</td>
<td>0,0372</td>
<td>7,44</td>
<td>94</td>
<td>0,0672</td>
<td>13,44</td>
<td>66</td>
<td>0,100</td>
<td>20,02</td>
<td>45</td>
</tr>
<tr>
<td>U-238</td>
<td>0,0398</td>
<td>7,95</td>
<td>94</td>
<td>0,0632</td>
<td>12,65</td>
<td>66</td>
<td>0,104</td>
<td>20,86</td>
<td>45</td>
</tr>
<tr>
<td>Th 230</td>
<td>0,0241</td>
<td>4,81</td>
<td>100</td>
<td>0,0554</td>
<td>11,09</td>
<td>64</td>
<td>0,07</td>
<td>13,74</td>
<td>72</td>
</tr>
<tr>
<td>Th 232</td>
<td>0,0270</td>
<td>5,39</td>
<td>100</td>
<td>0,0558</td>
<td>11,17</td>
<td>64</td>
<td>0,07</td>
<td>13,74</td>
<td>72</td>
</tr>
</tbody>
</table>

Remaining work

1. We will continue to develop rapid digestion methods (fusion, microwave digestion) for different matrices of soil and sediment samples.
2. Separation of actinides will be further examined for soil and sediment samples by extraction chromatography based on DGA resin. The high selectivity of DGA will probably make the preconcentration step unnecessary.
3. Feasibility of different α-source preparation procedures (electroplating, micro co-precipitation) will be examined for processing suitable actinides into multiple or single-element sources.
4. Different spectrum processing software programs (Hypermet, Genie2000) will be used for the evaluation of the measured spectra.

Related publications


IV. ENERGY AND ENVIRONMENTAL STUDIES
TESTING OF MoS$_{2-x}$O$_x$ 2D SURFACES IN ELECTROCATALYTIC WATER SPLITTING

József S. Pap, Dávid Lukács, Tamás Ollár, Levente Tapasztó, Antal Koós, Dávid F. Sranko, Zsolt G. Kerner

Objective

Our main scientific goal was to investigate the structure-reactivity correlations in electrocatalysts designed for the splitting of water. MoS$_2$ is a promising electrode modifying material to improve the effectiveness of the hydrogen evolving reaction. The oxidation of 2D MoS$_2$ crystals was shown to spontaneously occur upon ambient exposure at under-coordinated sites, such as edges and grain boundaries. By contrast, the oxidation of the defect-free basal plane has been predicted to be kinetically limited, conferring environmental stability to MoS$_2$ crystal surfaces. However, the basal plane affinity towards ambient oxidation has so far remained experimentally unexplored. Beside the in-house financing, the full project had support from the VEKOP 2.3.2-16-2016-00011 “Strategic research group for the challenges of renewable energy based power systems” project from July 2017.

Methods

We have prepared mechanically exfoliated MoS$_2$ single layers on atomically flat Au (111) substrates by a recently developed exfoliation technique. The exfoliated MoS$_2$ samples have been stored under ambient conditions (air, room temperature and ambient light) for periods of up to 1.5 years. Electrochemical measurements have been conducted on selected sample areas (0.4 - 0.8 mm diameter) of a single 2D MoS$_2$ flake supported by a 100 nm thick Au(111) film on a glass substrate. Control measurements on the same Au (111) substrate as well as on a Pt plate and a non-oxidised MoS$_2$ surface have been conducted in the same experimental configuration. To compare the performance of different samples in the Hydrogen evolving half-cell reaction (HER), linear sweep voltammetry was performed in a three-electrode configuration using 0.5 M sulphuric acid electrolyte at room temperature. Silver/silver chloride and Pt wire were used as counter and reference electrodes, respectively. Potential sweeps were acquired at a scan rate of 2 mV/s using a Bio-Logic SP-150 potentiostat (Fig. 1a, converted to Tafel plots in Fig. 1b).

Results

We found that a simple annealing of the MoS$_{2-x}$O$_x$ crystals under an H$_2$S atmosphere at 200°C for 30 minutes is able to fully restore the atomic structure of the pure 2D MoS$_2$ phase. The electrochemical measurement demonstrated a highly increased catalytic HER activity of the 2D MoS$_{2-x}$O$_x$ solid solution crystals, as compared to the reduced pure 2D MoS$_2$ phase, which manifested in a lower onset potential (Fig. 1a, red curve) and a reduced Tafel slope (67 mV dec$^{-1}$, Fig. 1b). This oxidation process enables the chemical modification of single atomic sites of 2D crystals, opening new routes towards their efficient defect engineering. An important example is that the O substitution sites present all over the basal plane substantially increase the catalytic activity of the 2D MoS$_2$ crystals for electrochemical H$_2$ evolution reaction. In line with the above results, in hydro-desulfurization catalysis we also showed that the exchange of mobile sulphur atoms plays a crucial role in creating the catalytically active sites (or at least one type of the active sites) on MoS$_2$ surfaces.

Figure 1: Catalytic activity of 2D MoS$_{2-x}$O$_x$ for hydrogen evolution. Linear sweep voltammetry curves (a) and the corresponding Tafel plots (b) for: Au substrate, MoS$_2$ single layer, MoS$_{2-x}$O$_x$ single layer (1 year old), and Pt substrate, revealing a significantly higher catalytic activity of the 2D oxy-sulfide phase as compared to the pure MoS$_2$ phase, attributed to the novel catalytically active O substitution sites emerging on the basal plane during the oxidation process (RHE = Reversible Hydrogen Electrode).

Related publications


Understanding of the Dry Reforming Reaction for the Development of Novel Catalysts

Ferenc Somodi, Miklós Németh, Anita Horváth

**Objective**

The catalytic dry reforming reaction is of great importance because it yields hydrogen and carbon monoxide as reaction products in an equimolar ratio (dry reforming, (DRM): \( \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \)) from sources such as, for example, a cleaned biogas. The catalytic properties of our novel samples designed for this reaction were explored further this year. There were two Ni-containing catalyst systems to study: i) the active metal was modified with indium (NiIn/SiO\(_2\)) or platinum (NiPt/ZrO\(_2\)) and ii) the ZrO\(_2\) support was modified with Na\(_2\)O.

**Methods**

Besides the existing catalysts, which were prepared by an impregnation method, sol adsorption or deposition precipitation techniques, a bulk Na\(_2\)ZrO\(_3\) support was newly prepared from NaHCO\(_3\) solution and ZrO\(_2\) powder followed by high temperature treatments. Structural investigations were carried out by X-ray powder diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM). Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was applied to detect the surface-adsorbed species in the presence of CO, CO\(_2\) or a dry reforming mixture under different temperature conditions. Temperature-programmed dry reforming experiments were done in a plug flow reactor in excess methane. Subsequent temperature programed oxidation (TPO) was carried out to quantify the deposited carbon. Decomposition of methane was investigated by mass spectrometry assisted pulse chemisorption experiments at 600 °C on freshly reduced and on carburized Ni/SiO\(_2\) and Ni-In/SiO\(_2\) dry reforming catalysts.

**Results**

Concerning the Ni or NiPt/ZrO\(_2\)(Na\(_2\)O) systems, our detailed DRIFTS experiments in CO or CO\(_2\) flow showed that CO adsorption on the H\(_2\)-precovered catalysts (CO+H\(_2\) surface reaction) resulted in the formation of formates around 300 °C. However, their bonding strength (wavenumber), decomposition route (to carbonates) and speed was markedly different on the samples. It can be suggested that when the surface-bonded formate’s C-H vibration is as low as 2830–2800 cm\(^{-1}\), the sample has long term stable DRM activity or coke free operation due to the localized 0.6 wt% Na\(_2\)O promotion.

Based on our earlier results, nanosize Na\(_2\)ZrO\(_3\) islands around Ni (or rather the dynamic Na\(_2\)O-ZrO\(_2\)-Ni/NiO-H\(_2\) interface) have a decisive role in the effective coke removal from Ni. This is why 3%Ni/Na\(_2\)ZrO\(_3\) catalysts were prepared. The XRD, catalytic and DRIFTS results showed that the presence of 3-5 %Na\(_2\)CO\(_3\) residue (from the support preparation) completely deactivates the catalyst and blocks the Ni surface of big, 100 nm Ni particles. The removal of Na\(_2\)CO\(_3\) residue was successfully achieved by washing of the support. However, during the Ni introduction step, it could be re-formed again – although in a minute amount – on the surface, while the required bulk Na\(_2\)ZrO\(_3\) phase disappeared, and the catalyst had moderate dry reforming activity without coke formation. DRIFTS experiments on this washed sample firmly ascertained that the sodium content causes the 1800 cm\(^{-1}\) band of bridged CO on Ni and the low wavelength formate C-H band (weak C-H bond) which can be decomposed easily.

Concerning our novel, coke tolerant, indium promoted system, DRIFTS experiments gave the following results. During CO chemisorption at room temperature, linear monocarbonyls, unstable tetracarbonyls and bridged carbonyls bound to nickel were detected on Ni/SiO\(_2\) while only linear monocarbonyls were seen on NiIn/SiO\(_2\). The bimetallic character of the surface was reflected in the lower wavelength of the linearly adsorbed CO molecules (at around 2025 cm\(^{-1}\)) which were present on the hydrogen-precovered surface at 300 °C with a surprisingly high concentration. Using a DRM mixture, the NiIn surface kept CO molecules up to 500 °C, while there was no metal-bonded CO on Ni/SiO\(_2\) above 400 °C, probably due to the formation of nickel carbide. CO chemisorption after the reaction revealed clean but somewhat segregated NiIn sites on the bimetallic sample, in similar concentration as before the reaction, while on Ni/SiO\(_2\) the available Ni surface significantly decreased. The presence of NiIn sites was ascertained on the NiIn/ZrO\(_2\) sample as well. The catalytic activity of this sample was lower, but coke was not formed during the reaction.

Next, a methane activation step was investigated on our In-promoted catalysts. The mass spectrometry assisted, methane pulse experiments at 600 °C on freshly reduced and on carburized Ni/SiO\(_2\) and Ni-In/SiO\(_2\) dry reforming catalysts revealed that complete methane decomposition with stoichiometric hydrogen production on freshly reduced Ni/SiO\(_2\) took place, while strong hydrogen chemisorption and partial methane decomposition was observed on Ni-In/SiO\(_2\). Hydrogen production decreased on both carburized catalysts and dissociative methane chemisorption without hydrogen formation was observed on the bimetallic catalyst. This difference in methane activation might be one of the reasons for the absence of coke on the bimetallic catalyst during dry reforming of methane.

**Remaining work**

The related EK 161 project will be finished. The topic will be continued with an outlook to the related CO\(_2\) utilization routes. Publications in preparation will be submitted soon.
Related publications


**Effect of Preparation and Support of Au-based Catalysts on Selective Oxidation of Alcohols**

Gergely Nagy, Dávid Srankó, György Sáfrán, Sándor Stichleutner, László Borkó, Antal Tungler, Zoltán Schay, Ferenc Somodi, Károly Lázár, Andrea Beck

**Objective**

As a continuation of the investigations and development of supported Au-containing catalysts for aerobic selective oxidation reactions, the effect of the preparation method and the support was studied in the case of monometallic Au and bimetallic Au-Cu and Au-Ag systems in aerobic benzyl alcohol or glycerol oxidation. The work was done in collaboration with the Italian Istituto di Scienze e Tecnologie Molecolari (CNR-ISTM) and Frascati National Laboratories (INFN), and the Chinese State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics.

**Methods**

Catalysts were prepared using various supports by the sol immobilisation method (SOL) and compared with ones produced by solvated metal atom deposition (SMAD). Catalytic tests were performed in benzyl alcohol (BnOH) oxidation in toluene, cyclohexane or xylene solutions without or with base (K₂CO₃) addition, and glycerol (Gly) oxidation in aqueous solution with base addition (NaOH). For structural characterisation (HR)TEM, XPS, XAFS techniques and CO adsorption (followed by DRIFT spectroscopy and measured by QMS), CO₂-TPD and NH₃-TPD measurements were used.

**Results**

In glycerol oxidation, increased activity and different selectivity (favoured transformation of glyceric acid to tartronic acid) of SOL prepared AuAg/Al₂O₃ (Au/Ag=4/1 atomic ratio) and Au/Al₂O₃ as compared to the ones made by SMAD was established. This was related to both the larger particle size and also to the higher surface enrichment of Ag on AuAg nanoparticles (NPs) on the SMAD samples, which further increased after calcination treatment. Additionally, Ag was more resistant to oxidation in the SOL sample, indicating its modified electronic state resulting from the more extensive interaction with Au. The Au and AuAg NPs were more stable against sintering in the SOL than in the SMAD derived catalysts. The stabilizing agent residues of the SOL catalysts slightly hampered the activity, and affected the selectivity. After its removal by calcination the tartronic acid selectivity further increased, accompanied by a reduction of glyceric acid and C-C cleavage products. The bimetallic SOL sample was more active than the monometallic Au/Al₂O₃ (due to the promoting effect of Ag) with higher tartronic acid, but also C-C cleavage product selectivity. [1, 4, 7]

The large effects of the type and structure of the carbon support (Vulcan-XC72R, Norit GSX, X40S) were observed in glycerol oxidation for Au/carbon catalysts prepared by both SOL and SMAD methods, providing similar mean Au NP size (2.5-3.9 nm) (except Au/X40S_SMAD of 7.1 nm mean diameter). In the case of the different supports which vary in surface area, pore size, functionalization and graphitization degree, the activity order of Au/Vulcan>Au/Norit>Au/X40S was found in both sets. All the SOL samples were more active, than the corresponding SMAD ones. [2]

Alumina and carbon (Vulcan) supported Au-Cu bimetallic systems produced by the SOL method with Au/Cu=1/4, 1/1, and 4/1 atomic ratio were compared in benzyl-alcohol oxidation, without any pre-treatment in a cyclohexane solution, at 120°C and with (Au+Cu)/BnOH=1/500 molar ratio without base addition. In contrast to earlier results on the similarly prepared AuCu/Al₂O₃, Au/Cu=1/1 with differing conditions: toluene solvent, 80°C, Au/BnOH=1/2000, there was no poisoning/deactivation detected, but the synergetic effect revealed earlier for Au/Cu=1/1 was confirmed, and found also for Au/Cu=4/1 both on alumina and Vulcan supports, and in the case of AuCu/Al₂O₃ for Au/Cu=1/4 as well. (The corresponding monometallic Cu-catalysts had negligible or no activity.) Approaching the 100% conversion, the only detected product benzaldehyde started to transform further to benzoic acid. The same AuCu, Au and Cu NPs originated from the same precursors, respectively, were all more active on alumina than on Vulcan support. [3, 5]

Au catalysts supported on non-reducible oxide (SiO₂, Al₂O₃, MgO, MgAl₂O₄) and non-oxide (hydroxyapatite, HAP) supports with different basicity and acidity were studied in benzyl alcohol oxidation (xylene solvent, 50°C, Au/BnOH =1/1300). According to the CO₂-TPD and NH₃-TPD measurements MgAl₂O₄ and HAP contained both basic and acidic sites of different strength, Al₂O₃ stronger acid and weaker basic, MgO only basic, while SiO₂ had neither basic nor acid sites. The average size of the SOL derived Au particles were between 2.4 and 2.7 nm on the calcined samples (where no protecting agent was left around Au NPs), except for Au/Al₂O₃ (1.7 nm) and Au/MgO (6.5 nm). In base free reactions (where the catalysts quickly deactivated), the purpose of the activity was Au/MgAl₂O₄>Au/Al₂O₃>Au/MgO>Au/HAP>Au/SiO₂=0. With base addition (where no deactivation was observed) the differences between the larger activities were smaller, but their order remained similar. The stronger basicity seemed to favour the reaction, while the acidity affected the selectivity by enhancing slightly the benzyl benzoate selectivity (16-22% vs 10-12% at about 70% conversion). [6]

**Remaining work**

The publication of the unpublished results.
Related publications


BIOMASS CONTENT DETERMINATION OF BIOFUELS BY $^{14}C$ LIQUID SCINTILLATION COUNTER (LSC) METHOD

Tamás Korányi

Objective

Biomass content determination of biocarbon - fossil carbon containing mixtures (biofuels, cellulose, lignocellulose and lignin derivatives) by radiocarbon ($^{14}C$) liquid scintillation counting (LSC).

Methods

Two kinds of LSC methods were/will be applied:

- **Direct counting**: The product mixture is dissolved directly in a scintillation cocktail and its biogenic carbon content was measured in LSC equipment. This method is only applicable using colourless or slightly coloured samples.
- **Sample combustion and carbon dioxide trapping**: Samples will be burned using air in a burning oven and the produced carbon dioxide will be trapped in a sodium hydroxide solution. The precipitate will be dissolved in the scintillation cocktail and measured by LSC. This method is under development, but it is not working yet.

Results

Our Belgian partners (Prof. Bert Sels et al., Katholieke Universiteit Leuven) produced biogasoline by valorizing (hemi)cellulose pulp into light naphtha using a two-phase ($H_2O : organic$) catalytic slurry process. They directly integrated this process into existing light naphtha petrorefinery processes. They measured the biomass content of their biogasoline – fossil gasoline mixtures by gas chromatography (GC) (Table 1), but this methodology is unreliable because of neglecting some alkane products. We monitored the carbon origin of some of their samples by our direct LSC method and revealed the missing biocarbon content (Table 1). Due to the novel direct integration approach of bio-enriched gasoline production, we published these results in the prestigious journal Nature Energy [1].

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Fossil solvent</th>
<th>Biomass-derived content determined by GC (wt%)</th>
<th>Biomass-derived content determined by LSC (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>Petroleum ether</td>
<td>10.7</td>
<td>12.1</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Petrol</td>
<td>15.6</td>
<td>18.0</td>
</tr>
<tr>
<td>Carbohydrate pulp</td>
<td>Petrol</td>
<td>6.6</td>
<td>11.8</td>
</tr>
</tbody>
</table>

We started to determine the biocarbon content of catalytically converted biomass (cellulose, lignocellulose and lignin) samples of our Dutch colleagues (Prof. Katalin Barta et al., University of Groningen). Some promising preliminary results were obtained, but due to the low biocarbon content and the disturbing colour of most of their samples, using the sample combustion and carbon dioxide trapping method will give more reliable results for most of the Dutch samples.

Some other LSC related results will also be reported in another project (126_2018).

Remaining work

Building of the sample combustion and carbon dioxide trapping experimental setup has been started, but due to a delayed reconstruction work of our laboratory, we could not yet finish this work.

Related publication

SOD-LIKE ACTIVITY AND CYTOTOXICITY ASSESSMENT OF NEW ANTIOXIDANT SYSTEMS

Inna Székács, József S. Pap, Krisztina Kovács, Tünde Tóth, Róbert Horváth

Objective

Superoxide dismutase (SOD) is an enzyme family that regulates reactive oxygen species (ROS) in living organisms. Malfunction of SODs leads to a harmful level of oxidative stress on the body. For therapeutic purposes, artificial complexes with catalytic antioxidant activity are envisioned as SOD-mimics to fix the regulation of ROS. Our objectives were to measure the SOD-like activity of Cu(II) complexes based on a phosphonate substituted SALAN-type ligand by direct and indirect methods, and rationalize their in vitro effect on cells, considering the coordination modes and the redox behaviour.

Methods

The complexes were characterized by molecular (UV-visible, Circular Dichroism, Electron Paramagnetic Resonance, X-ray Absorption and Extended X-Ray Absorption Fine Structure (EXAFS)) spectroscopy, Electrospray Ionization Mass Spectrometry (ESI-MS), electrochemistry and geometry optimization using Density Functional Theory (DFT) calculations. SOD-like activity has been determined by the McCord-Fridovich method and directly by pulse radiolysis. Cytotoxicity has been studied on living cells with the optical biosensor Epic BT. Determination of the cell viability was done by using HoloMonitor M4.

Results

All characterizations were done in aqueous solution at physiological pH (7-8). ESI-MS (Electrospray Ionisation Mass Spectrometry) showed an equimolar [Cu(L)] complex upon addition of Cu²⁺ to L (L = (R,R)-1,2-cyclohexylenediamine-di-(R,R)-(2-hydroxyphenyl)-methylphosphonic acid) up to 1:1 molar ratio. Results from spectroscopy suggest a [2N,2O] coordination mode including one phenolate oxygen donor for each Cu²⁺ ion. The geometry optimized structure by DFT (Fig. 1) accords with this assignment. The Cu···Cu distance is 4.85 Å, the Cu–N bonds are ~2.00 Å, the Cu–Ophenol bonds are 1.94 Å, while the Cu–O phosphonate bond lengths are 2.03 Å and 1.99 Å, respectively for the two centres. In addition, DFT predicts that the fourth positions are occupied by aqua ligands at 2.05 and 2.02 Å from the cupric centres. The average of the optimized distances (~1.99 Å) is in line with the Cu–N(O) = 1.98 by EXAFS (Extended X-ray Absorption Fine Structure).

The Cu²⁺/²⁻ formal potential (E°) under the reaction conditions is an important thermodynamic criterion of the SOD-like behaviour. The catalytic disproportionation process involves redox reactions between the reduced as well as the oxidized complex forms and O₂⁻. The E° for both complexes is in the appropriate range to expect SOD-like activity.

The k McCF (M⁻¹s⁻¹) rate constants derived from the McCord-Fridovich test imply that [Cu₂(L)] is an outstandingly active O₂⁻ scavenger, but [Cu(L)] also ranks among the better mimics. However, both lag behind the natural CuZn SOD enzyme. The rate constants were in agreement with those determined by pulse radiolysis, where the decay of O₂⁻ was directly monitored at 270 nm under real catalytic conditions.

The effects of the Cu-complexes and Cu²⁺ on the functional state of surface-adhered living cells and on the cell adhesion process were explored in a serum-containing cell culture medium using an Epic BT optical biosensor. This device is usable for a label-free screening of the comprehensive effects of xenobiotics on the biological status of cells (e.g., cell viability, cell adhesion processes, cell integrity, signalling) [1]. The 2 h long measurements show no differences between the cells treated with [Cu₂(L)], [Cu₂(L)] or Cu²⁺ and the control. However, the exposure to [Cu₂(L)] and Cu²⁺ at 400 µM after 24 h of incubation leads to cell apoptosis. Time-based changes of cell proliferation and morphology parameters under the treatment with [Cu₂(L)], [Cu₂(L)] and Cu²⁺ at 400 µM were monitored for 72 h using a HoloMonitor M4 placed into an incubator. Control cells and cells treated with [Cu(L)] showed a normal morphology and proliferated exponentially. In contrast, [Cu₂(L)] and Cu²⁺ caused a ~4 h delay in cell proliferation. Surprisingly, Cu²⁺ stimulates cell proliferation for 8 h, but then the proliferation is terminated. Changes in cell morphology begin after ~14 h of incubation with [Cu₂(L)] and Cu²⁺ and intensify over time, and disrupted cellular functionality leads to apoptosis. In summary, no notable cytotoxicity was registered for Cu-complexes at the reasonable concentration level (10-20 µM), but [Cu₂(L)] at 400 µM causes cell apoptosis. Treatment with [Cu(L)] did not show visible cytotoxicity even at high concentrations which makes it a potential candidate for antioxidant therapies [2].

Remaining work

The work was completed and a manuscript is in progress. Studies on other antioxidant complexes are among our plans.
Related publications


**LONG-TERM PROSPECTS AND DEVELOPMENT OPPORTUNITIES OF THE DOMESTIC ELECTRICITY AND HEAT SUPPLY**

*Endre Börcsök, Ágnes Gerse*

**Objective**

In the context of this research related to the long-term development of the domestic electricity and heat supply, we addressed three main areas in 2018. As first area of interest, we focused on the heat sector by formulating the search for an optimal heat and domestic hot water supply portfolio of Budapest as a multiobjective optimization problem involving economic, environmental and human health aspects. Two additional fields of research were related to the electricity sector: the development of a regional electricity supply model and a country-level wind power production model.

**Methods**

A multiobjective optimization methodology was applied in the context of the optimal heat supply portfolio of Budapest. The techno-economic assessment was complemented by monetizing the environmental impacts and the influence of the technology choices on human health. Among the technology options, the long-distance heating from Paks Nuclear Power Plant has also been considered and evaluated. The methodology was based on monthly heat demand profiles, distinguishing among three typological groups of buildings and optimizing the set and installed capacity of heating technologies for each of these groups. Two different approaches have been applied to the analysed multiobjective optimization problem involving three objectives. According to the first approach, the three objective functions were encompassed in an overall objective function by monetization and the problem was solved as a linear programming (LP) formulation of a simple transportation problem; while the second approach used a multiobjective optimization method.

For the electricity sector, the regional electricity supply model was implemented in Antares (A New Tool for Adequacy Reports and Economic Simulations), where we gratefully acknowledge the support of RTE, transmission system operator for electricity in France. Reflecting the complexity of the electric power system, a large set of input data was required to run the model, including power plant characteristics, cross-border transmission capacities, demand and generation patterns. By solving the unit commitment and the economic dispatch problem as a constrained least-cost optimization problem for the power system, resulting time series for cross-border exchanges and power plant generation are available at an hourly scale. Providing model-based-time series for simulations, the wind power production model for Hungary uses a reanalysis-based modelling approach. The hourly aggregate wind energy production is modelled by converting gridded hourly wind speed data into aggregate power output via the power curves of the wind turbines where hourly wind speed time series were retrieved from the ERA5 reanalysis archive, released by the European Centre for Medium-Range Weather Forecasts.

**Results**

The results of heat supply optimization show that single family houses mostly rely in this simulation on ground and air source heat pumps while their winter peak demand is covered by heat from natural gas. The optimal heat supply of medium-scale and large-scale multi-flat buildings is based on district heating to a large extent where municipal solid waste and biomass are the base-load fuels and nuclear cogeneration appears in the intermediate range. For peak supply, heat production from natural gas was selected as an optimum with different configurations: individual heating systems are the most suitable for medium-scale multi-flat buildings while centralized supply via district heating is the best option for large-scale multi-flat buildings. The regional electricity supply model was run and calibrated for eight countries. Although the main trends in the structure of generation and cross-border electricity exchanges are well reflected, modelling results may substantially differ when compared to actual market data given the limitations in the methodology. In the part of work related to wind energy, the availability of sufficiently long time series with virtually unchanged wind turbine fleet made Hungary an ideal test case for the applicability of ERA5 data for wind power modelling. The performance of the model has been evaluated against multiple criteria where hourly data were closely correlated to data from measurements.

**Remaining work**

We would like to include further aspects of analysis in addition to the three criteria already included in the heat supply optimization model and assign weight factors to the set of criteria. The regional electricity supply model is planned to be extended to additional countries along with the improvement of data quality, while the further work on the wind power generation model could focus mainly on the model-based assessment of future national wind power development scenarios.

**Related publications**


Figure. 1: Optimal heat supply portfolio for the Residential Sector in Budapest modelled by monetized value
**Effects of Heterogeneity in Power-Grid Network Models**

Géza Ódor, Bálint Hartmann

**Objective**

Power-grids are becoming more and more heterogeneous as renewable small (solar, wind, geothermic) suppliers are connected. Therefore, the danger of desynchronization may increase. We have studied the effects of topological and intrinsic (node connection strength) disorder on the second order Kuramoto model with respect to simple homogeneous lattices. Our aim was to provide a description of the desynchronization transition, determine the fluctuations and the heavy tailed failure avalanche distributions, reported on several large blackout events. We have planned to explore possible Griffiths phases and to provide a measure of danger as the function of stochastic elements connected.

**Methods**

We compared the phase synchronization transition of the second order Kuramoto model, a basic model describing AC electric networks, on 2D lattices and on large synthetic power-grid networks generated from real data. While admittance matrix of the transmission network is based on a real-life example (the Hungarian power system), matrix of the distribution network is the result of synthetic grid modelling. Equations of the second order Kuramoto model for the phases $\Theta_i$ and the global coupling control parameter $K$ have been analysed numerically, using 4th order Runge-Kutta differential solvers. Here we introduced quenched heterogeneities, via the $\omega_i$ intrinsic frequencies of the $N$ nodes, connected via the $A_{ij}$ admittance matrix. For the inertia parameter we used $\alpha = 1,3$ and we also considered the addition of Gaussian as well as exponentially distributed noise terms. We have measured the global phase synchronization order-parameter and determined the static/dynamic phase transition behaviour. We have also determined the distribution of the duration times from fully synchronous ($R = 1$) to disordered ($R = 1/N^{1/2}$) states, by random sample averaging.

**Results**

As the continuation and extension of our 2017 project, we investigated the effects of distributed power supply elements. For the traditional electric system, we used binary $\omega_{i,0}$ frequency distributions, with generators in the high voltage nodes $\omega_{i,0} = 10 + \rho_G$ while in the other consumer nodes: $\omega_{i,0} = -1 + \rho_G$, where $\rho_G$ is a unit variance Gaussian random variable. To model a distributed/renewable system we applied for sources: $\omega_{i,0} = 2.5 + \rho_G$ and for consumers: $\omega_{i,0} = -1 + \rho_G$ randomly. Using adiabatic quench, we determined the steady state synchronization as the function of the global coupling (related to the maximum transmitted power between nodes). As the Figure shows, we obtained higher synchronization in case of the distributed/renewable model than in case of the traditional setup. We submitted this new result and a summary of the talk we presented at MTA in May to Fizikai Szemle, while we published the previous year results as: Géza Ódor, Bálint Hartmann, *Heterogeneity effects in power grid network models*, Phys. Rev. E 98 (2018) 022305. We presented the results by a talk on the AMCOS 2018 synchronization conference in Barcelona and the usage of GPU-s (Graphics Processing Units) for speeding up calculations at the GTC2018 conference in San Jose.

**Remaining work**

We would like to better understand the stability of conditions of power-grids by using more detailed models and to compare our results with ENTSO (European Network of Transmission System Operators for Electricity) power failure data.

**Related publications**


CONDITIONING AND FINAL DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTE

Margit Fábián, Ottó Czömpöly, Felicián Gergely, János Osán

Objective

At the end of the nuclear fuel cycle high level radioactive waste (HLW) is generated that has to be disposed of in a safe way. Vitrification, where actinides from HLW materials are melted into a glassy form, is a feasible and widely accepted conditioning method. A promising borosilicate matrix glass composition was developed in the previous years. Lanthanides, chemically modelling the actinides present in the waste, were added to the matrix in the form of CeO$_2$, Nd$_2$O$_3$ and Eu$_2$O$_3$. The structural characterization of the loaded glass is important in order to determine the immobilization rates of the HLW. Previous neutron diffraction (ND) measurements, combined with Reverse Monte Carlo (RMC) simulation, revealed that lanthanide atoms can effectively incorporate into the matrix glass structure. In order to complement and support the structural studies, we aimed to investigate the oxidation state and the local environment of the incorporated lanthanide ions.

The final disposal of HLW is generally planned in deep geological repositories. The Boda Claystone Formation (BCF) is considered as the potential host rock of the future HLW repository in Hungary. We intended to study the retention capabilities of the argillaceous host rock as a natural barrier through a series of macroscopic experiments quantifying sorption of key radionuclides at a constant pH, and a solid-to-liquid (S/L) ratio at different equilibrium concentrations.

Methods

For studies related to vitrification of HLW, two series of Ce-, Nd- or Eu-containing glassy samples were prepared and investigated. The composition of the borosilicate matrix (denoted as Matrix) is 55SiO$_2$·10B$_2$O$_3$·25Na$_2$O·5BaO·5ZrO$_2$. The composition of the glassy specimens of the two series are 90wt%[Matrix]+10wt%X, and 70wt%[Matrix]+30wt%X, where X stands for CeO$_2$, Nd$_2$O$_3$ or Eu$_2$O$_3$. Glassy samples were prepared by the melt-quenching technique.

The lanthanide-containing amorphous samples as pressed pellets were investigated using X-ray absorption spectrometry (XAS). Measurements were performed at the L$_2$ and L$_3$-edge of Ce and Nd, and at the L$_3$ edge of Eu. Nuclear Magnetic Resonance (NMR) and Raman spectroscopy were also used to get complementary information on the boron environment.

Sorption on the host rock of the waste repository of radionuclides that may be released from the radioactive waste was modelled by laboratory experiments. A series of macroscopic experiments were performed for Cs$^+$, Ni$^{2+}$ and Eu$^{3+}$ ions on five different core samples originating from a recent drilling in BCF. The argillaceous rock samples were ground to less than 63 µm grain size. Sorption isotherms were measured at pH 8.0 via inductively coupled plasma mass spectrometry (ICP-MS) analysis of the liquid phase separated by centrifugation or ultrafiltration.

Results

Structural characterization of the designed model glasses was completed with NMR, Raman spectrometry and XAS measurements verifying atomic level integration of lanthanides into the matrix-glass structure [1]. XAS experiments revealed that although cerium was added to the glass structure as Ce$^{4+}$, it integrates into the glass structure as Ce$^{3+}$, while europium remained in the originally added trivalent form. It was found that Nd$^{3+}$ and Eu$^{3+}$ ions do not form clusters within the glass structure, even at high concentrations, indicating that these lanthanides are homogeneously dispersed, hence providing a high stability of the compact glassy structure.

Partition coefficients ($R_d$) between the solid and liquid phase for the selected ions correlate well to the illite and chlorite content of the recent BCF core samples, supporting the assumption that sorption mainly occurs on clay minerals [2]. The $R_d$ values determined by ICP-MS for Cs$^+$ are in line with earlier investigations carried out on core samples from past drillings using the radiotracer method.

Remaining work

Leaching of radionuclides from the glasses which model vitrification of HLW will be studied. Macroscopic sorption experiments on the new core samples of BCF will be complemented with microscopic investigations.

Related publications


CHARACTERIZATION OF ATMOSPHERIC AEROSOL PARTICLES HAVING AN ENERGY GENERATION ORIGIN

János Osán, Csenge Dian, Endre Börcsök, Levente Illés, Viktória Kovács-Kis, Szabina Török

Objective

In recent decades European countries have made progress in reducing particulate air pollution due to concern about their health and climate effects. However, contrary to industrial sources, biomass combustion emissions are increasing in Eastern Europe. It has been shown that such particles contribute more than 40% of the fine particulate matter even in suburban and urban areas in Eastern and Central Europe. These results were obtained from a statistical analysis of large datasets of daily-taken samples characterized with an extensive set of analytical methods.

The aim of the present work was the identification of the sources based on investigation of samples collected for a few hours using a limited number of non-destructive analytical methods. In order to achieve this goal, a special cascade impactor sampling method was developed allowing simultaneous collection of samples which are reliable for use with different analytical methods. Total-reflection X-ray fluorescence (TXRF) is a very sensitive method for elemental analysis of the deposited particles. If Si wafers are used as collection substrates, the same samples can be investigated by scanning electron microscopy (SEM) without a carbon coating. Transmission electron microscopy (TEM) investigations become possible if the impactor is able to sample on TEM grids.

Methods

For size-fractionated sampling of atmospheric particulate matter, a 9-stage May type cascade impactor was used covering a wide size range of 70 nm to 16 µm, including part of the ultrafine particles. Impactor plates have been redesigned to hold 20×20 mm² Si wafers and TEM grids.

Samples were collected in suburban Budapest (Hungary) and in urban Cassino (Italy). Only the range of the fine fraction (70 nm to 2.5 µm) was considered for this study. Sample collection times varied from 20 min to 4 hours. Elemental analyses of the deposited particles were performed using TXRF in laboratory and using synchrotron radiation (SR) at Elettra (Trieste, Italy). Individual particles were visualized by SEM and TEM.

Results

Measurements of test samples collected at two sites with different source profiles revealed that cluster-like soot and spherical organic particles can be sampled effectively in the 70-200 nm size fraction that is characteristic for both traffic and biomass combustion sources.

Urban and suburban sites are affected by both traffic and biomass combustion sources with different temporal characteristics [1]. In the 70-180 nm size range carbonaceous particles were found to be the most abundant as observed by SEM and TEM. TXRF was used to distinguish between traffic end-of-pipe (internal combustion engine) and biomass fuel burning sources based on the potassium (K) concentration [2]. In the 180-300 nm fraction the carbonaceous particles could be mostly related to biomass combustion. The K Ka signal in this fraction was highest in Budapest during winter, while in Cassino (Italy) even in the summer period the K Ka signal was above the average of Budapest. The reason for that is the intense use of wood in cooking stoves.

Remaining work

Further investigation of the collected samples is planned in order to obtain information on molecular composition of fine and ultrafine particles using Raman spectroscopy and SR based X-ray absorption spectrometry.

Related publications


Strategic Research Group for the Challenges of Renewable Energy Based Systems

Bálint Hartmann, Attila Kazsoki, Lilla Visnovszky, Bálint Sinkovics, Viktória Sugár

Objective

The primary aim of the second year of our research was to examine the possibilities of distribution network modelling, especially at medium voltage levels. The unification of data provided by different sources was to be carried out, and algorithms of complex network analysis were necessary to implement in MATLAB environment. Another aim of the year was to create a forecasting algorithm for solar photovoltaic electricity production. The model was based on the Bird clear-sky model, which has been corrected with various environmental and location parameters.

Methods

Grouping of medium voltage distribution network topologies was done using principal component analysis and k-means clustering. Solar photovoltaic electricity production forecasting uses a combined physical model and a neural network that is relying on environmental parameters.

Results

Topological data were received for six distribution system operator areas. In the case of two areas, only representative models were available, while for the remaining four areas, complete network data was provided by the distribution system operator. Unification of the datasets were carried out and a consistency check was performed. This revealed minor errors with two datasets, which necessitated further consultation with the data providers. For the distribution areas without errors, topology of 20 sample networks were available, representing 4 regions. For each feeder number of nodes, the average node degree, clustering coefficient and characteristic path length were calculated. The principal component analysis function of the Minitab 18.0 statistical software was used to identify the most valuable data of the underlying structure. Two principal components with the highest eigenvalue were selected as input for k-means clustering. The optimal number of clusters was determined, and representative networks of the resulting four clusters have been constructed.

[Figure 1: Representative networks of cluster 1 and 2]

Learning and testing of the physical model-based neural network used for the solar photovoltaic electricity production forecast was carried out using historical data recorded at the Centre. Input data of the neural network were rescaled to improve convergence times. Backpropagation learning was used, which was verified in each cycle. Environmental parameters used for the model were recorded with 15-minute time resolution and included ambient temperature, cloud cover, wind speed and snow cover.

Remaing work

The research project has a span of four years; the focus of the third year is the preparation of stochastic simulations.

Related publications

REDUCTION-OXIDATION EQUILIBRIA IN BODA CLAYSTONE MINERALS DETERMINED FROM Fe³⁺/Fe²⁺ RATIOS

Károly Lázár, Sándor Stichleutner, Zoltán Máthé*

Objective

Boda Claystone Formation (BCF) is considered as a potential repository site for high level nuclear waste in the near future. Migration of various radionuclides in BCF samples have extensively been studied in our laboratories previously. Possible influence of redox processes on migration of certain radionuclides was exposed recently. Thus, as a representative indicator of redox conditions, Fe³⁺/Fe²⁺ ratios were determined in samples acquired from different regions of BCF.

Methods

⁵⁷Fe Mössbauer spectroscopy was primarily applied and complemented with X-ray diffraction and optical microscopy. Samples were obtained from boreholes drilled in three different regions in south-west of Mecsek Mountains, i/ in the Western Anticline (BAF-2, BAT-14), ii/ in the Alpha-1 exploratory tunnel at about 1000 m below the ground level (Delta), iii/ and from the Gorica block (Ib-4).

Results

Beside direct redox properties, Fe³⁺/Fe²⁺ ratios in minerals can also be correlated with processes of diagenesis. In correspondence with a consent of experts the primary stages of formation of BCF had taken place in the Perm geological age under arid and oxidative conditions by desiccation of salty lakes starting roughly 250 My ago. In correspondence, the primary iron bearing minerals in BCF samples are hematite (Fe₂O₃), illite (Al,Mg,Fe)₃(Si,Al)₄(OH)₂[Si,O₁₀] and similar chlorite. These minerals were identified in various proportions almost in each samples. In some exceptional samples originated from regions formed under reducing conditions pyrite (FeS₂) and ankerite (Ca,Fe)CO₃ were dominant. Each of these minerals were unambiguously identified from their Mössbauer spectra as well.

Changes in the Fe³⁺/Fe²⁺ ratios were revealed in the illite component collected from different depths from BAF-2 borehole in the Western Anticline region. The greater is the depth the larger is the Fe²⁺ content in the illite/chlorite component. Simultaneously, proportion of hematite is decreasing with the depth (Fig. 1, left). Thus, formation of these two minerals was probably correlated during the genesis. In contrast, the Fe³⁺ contribution was dominant both in hematite and illite while Fe²⁺ was detected only in minor amounts (~ 10 %) in samples obtained from the other extended region, from Ib-4 driling in Gorica block (Fig. 1, right). Thus, the differences of formation of Fe²⁺ in the Western Anticline and in the Gorica block are clearly revealed in the Mössbauer spectra as well. Another process, weathering was also clearly reflected in Fe³⁺/Fe²⁺ ratios of samples collected from BCF samples from 23 – 70 m depths (BAT-14 borehole, the upper 0 – 22 m covering layer is permeable marl). The hematite content was constant, whereas the relative Fe³⁺ content in illite decreased from 30 % to 20% and, in reverse, the Fe²⁺ content increased from 4 % to 14 % with the increase of depth. The comparison of these samples demonstrates that illite is more sensitive to weathering processes than hematite. In samples collected from greater depths (~1000 m, Alpha-1 tunnel) minerals containing exclusively Fe²⁺ (pyrite and ankerite) were also identified [1].

Effects of oxidizing (perchlorate, hypochlorite, hydrogen peroxide) and reducing (hydroxylamine, formaldehyde, hydrazine) chemicals were also tested in slurries. Neither reduction nor oxidation was found, the Fe³⁺/Fe²⁺ ratios of minerals remained unaltered within a few weeks’ storage [2]. However, Fe²⁺ => Fe³⁺ redox process may contribute to immobilization of certain species (e.g. via Se⁴+ => Se⁰) in long term interactions with minerals of claystone as was demonstrated in our earlier reports related to migration studies.

Related publications


* Mecsekérc Environmental, Ltd.
PREPARATION AND CHARACTERIZATION OF NANOPARTICLE SYSTEMS DEVELOPED FOR PLANT NUTRITION EXPERIMENTS

Zoltán Klencsár, Sándor Stichleutner, Viktória Kovácsné Kis

Objective

Preparation and characterization of nanoparticle systems to be used in studies investigating the metal uptake and iron metabolism of plants.

Methods

Samples were prepared either via a hydrothermal process (HP) or via electric wire explosion (EWE). Except for the samples prepared via EWE, the various nanoparticle samples studied were prepared by Gy. Tolnai, Á. Ábrahám, A. Lengyel, Sz. Németh and R. Szalay. Powder X-ray diffractometry (PXRD), $^{57}$Fe Mössbauer spectroscopy ($^{57}$Fe MS), transmission electron microscopy (TEM), electron magnetic resonance (EMR) spectroscopy and inductively coupled plasma optical emission spectrometry (ICP-OES) were used to characterize the prepared nanoparticle systems. EWE and PXRD experiments were performed in cooperation with L.K. Varga at the Wigner Research Centre for Physics (Wigner RCP). ICP-OES measurements were performed by Z. May, whereas part of the TEM measurements were carried out in cooperation with L. Szabó, at the Research Centre for Natural Sciences, MTA. Magnetization measurements were performed by L. Kiss (Wigner RCP).

Results

Iron-oxide-hydroxide nanoparticles were prepared in the form of a nanocolloid suspension by the use of a precursor enriched in $^{57}$Fe. TEM measurements confirmed that the product included nanoparticles of iron oxide or iron oxide-hydroxide, with characteristic sizes of 5 nm and 20-30 nm. At the same time, $^{57}$Fe MS measurements performed at $\sim$80 K on the frozen suspension sample suggested that a large fraction of the iron still resided in the precursor material FeCl$_3$.

Nanomagnetites were prepared under different conditions, among others under an inert gas (N$_2$) atmosphere in order to achieve a high Fe$^{2+}$ ratio of the samples [1]. TEM measurements and corresponding selected area electron diffraction (SAED) patterns confirmed the presence of magnetite nanoparticles with a 10 nm characteristic size in the samples, along with some larger (ca. 50 nm) nanoparticles, which latter were identified as maghemite. Beside the iron oxides, TEM also revealed the presence of ferrihydrite or ferric oxide-hydroxide nanoparticles in the samples.

A new nanoparticle colloid suspension sample was created via EWE in water from a 0.2 mm diameter pure iron wire. Filtering the immediate product yielded on the one hand a pure, water-like liquid, and on the other hand a dense deposit of particles on the filter paper. Similar to the results of our previous experiment [2], the latter was shown to consist mainly of $\alpha$-Fe and Fe$_{x-}\text{O}$ (non-stoichiometric wüstite) by $^{57}$Fe MS, whereas TEM/SAED measurements confirmed the presence of nanoparticles (ca. 10-100 nm) in both sample fractions, with attributes akin to those of magnetite. ICP-OES also confirmed the presence of 0.067 mg/l of iron in the filtered colloid suspension.

The effect of aging was assessed on magnetite/maghemite as well as on Zn-ferrite nanoparticle powders. For the magnetite/maghemite powder, using $^{57}$Fe MS we were able to show that aging leads to the oxidation of an Fe$^{2+}$ iron species akin to that present in perfect magnetite, which confirmed that the original sample indeed contained magnetite [3]. In the case of crystalline and amorphous Zn-ferrite nanoparticle (ca. 5-6 nm) powders, TEM measurements and associated SAED patterns have confirmed the stability of both samples under ambient atmosphere over a year-long time period. For the latter samples the Zn:Fe atomic ratio was elucidated by ICP-OES measurements, and differences in the magnetic behaviour of the samples were reflected in magnetization measurements, the amorphous nanoparticles being characterized by an effective magnetic moment that is considerably lower than that of the crystalline sample.

Remaining work

The sample prepared with iron enriched in $^{57}$Fe needs further treatment in order to achieve a more complete transformation of the precursor material into the nanoparticles. Preparation, characterization and application of further nanoparticle samples are needed in order to explore the significance of specific material properties in influencing plant-nanoparticle interactions.

Related publications


EXPLORING THE IMPACT OF NANOPARTICLES ON PRODUCTIVITY, METAL UPTAKE AND IRON METABOLISM OF PLANTS

Zoltán Klencsár, Sándor Stichleutner, Viktória Kovácsné Kiss

Objective
Characterization of nanoparticle systems, and their application in studies investigating the metal uptake and iron metabolism of plants.

Methods
Nanoparticle samples were prepared via a hydrothermal process by Gy. Tolnai, A. Ábrahám, A. Lengyel, Sz. Németh and R. Szalay. Powder X-ray diffractometry (PXRD), $^{57}$Fe Mössbauer spectroscopy ($^{57}$Fe MS), transmission electron microscopy (TEM), electron magnetic resonance (EMR) spectroscopy and inductively coupled plasma optical emission spectrometry (ICP-OES) were used to characterize the prepared nanoparticles. PXRD experiments were performed in cooperation with L.K. Varga at the Wigner Research Centre for Physics (Wigner RCP). ICP-OES measurements were performed by Z. May, whereas part of the TEM measurements were carried out in cooperation with L. Szabó, at the Research Centre for Natural Sciences, MTA. Plant growth experiments were performed at the Department of Plant Physiology and Molecular Plant Biology of the Eötvös Loránd University.

Results
Low-temperature $^{57}$Fe Mössbauer spectroscopy measurements were performed on three different frozen suspensions of ferrihydrite/hematite nanoparticles, prepared by using different surfactant materials. The measurements revealed that more than 2/3 of all iron atoms is situated in ferrihydrite in the samples which also included hematite in different proportions along with a Fe$^{2+}$ species with parameters akin to those of FeCl$_2$$\times$2H$_2$O.

Zn oxide-hydroxide nanoparticle powder was prepared, and was investigated by the means of TEM and PXRD. TEM confirmed the presence of nanoparticles with a characteristic size of 50-100 nm, whereas we found the powder to contain a mixture of ZnO and Zn(OH)$_2$ by PXRD. Further oxidation of the sample resulted in ZnO powder with a wide particle size distribution in the submicron range.

An Al(OH)$_3$ nanoparticle colloid suspension was prepared and investigated by ICP-OES and TEM. The Al concentration of the suspension was found to be 481 mg/L by ICP-OES. TEM has implied that the sample is composed of poorly ordered platelets with a thickness of a few nm, and lateral dimensions in the order of several tens of nanometers.

Several different nanohematite/nanoferrithyrdate nanocolloid suspensions were tested in hydroponic cultures of iron deficient cucumber plants. The treated plants regenerated from iron deficiency in all cases at pH 5-6 but at pH 8.5 the nanomaterial suspensions deposited in the bottom of the pots as droplets. Cabbage plants were grown in iron deficient conditions (nutrient solution with CaCO$_3$ for foliar spray experiments. Mn-Zn-ferrite nanoparticle suspensions were used at 0.02-2 mM concentration to the plants as a spray, in conjunction with an additional surfactant, which resulted in a slight greening of the leaves.

In germination tests Mn-Zn-ferrite nanoparticle suspensions, used at 0.01, 0.1 and 1.0 mM concentrations, were found to stimulate germination of cucumber seeds. The results of germination tests performed with nano-Al(OH)$_3$ preparations applied in Petri dishes on white mustard seeds indicated that this nanomaterial does not have significant ecotoxicological effects on the germination of the seeds.

Remaining work
Further nanoparticle samples and plant growth experiments are needed in order to explore the significance of specific material properties in influencing plant-nanoparticle interactions.

Related publications


THE EFFECT OF CHEMICAL COMPOSITION OF CONCRETE ON ITS LONG-TERM PERFORMANCE IN IRRADIATED ENVIRONMENT

László Szentmiklósi, Katalin Gméling, Veronika Szinger-Szilágyi, Ildikó Harsányi, Boglárka Maróti, Tamás Fekete

Objective

During the construction of the new nuclear power plant units Paks II, the concrete structures will be made preferably from domestic raw materials. For this reason, we have to be prepared with suitable recipes of radiation-resistant, durable concretes with low activation susceptibility. The key to achieve that goal is the careful selection of the raw materials (gravel and sand) based upon the compositional data obtained by analytical and petrological methods. Analysis of the chemical composition of the concretes surrounding the reactor vessel is important, because they are exposed to high flux radiation, so their constituents might be substantially activated. Due to the neutron radiation, the high neutron-capture cross-section nuclides with short and long half-life become highly radioactive during the reactor operation time, while isotopes with long half-life remain radioactive for years following the reactor shutdown.

Methods

To achieve the research objectives, we sampled systematically the Hungarian gravel and sand mines. From four different regions, sixteen mines were sampled. From every selected mine four assorted (particle size: 0-4, 4-8, 8-16, 16-32 mm) and washed samples were collected. In addition, some admixtures (basalt, andesite, limestone) from Hungarian mines (Colas Északkő Kft.) and binders (different types of cements) from Vác and Beremend were chosen for analysis, in total 100 samples. After adequate preparation, samples were subjected to chemical elemental analyses (NAA + PGAA = NEAAA (Neutron-based element analysis and activation assessment) and XRF) and partly to petrographic (macroscopic, microscopic and heavy mineral) investigations. Prompt gamma activation analysis (PGAA) and instrumental neutron activation analysis (NAA) were performed at MTA EK, while X-ray fluorescence (XRF) measurements were done at SZIKKTI Laboratory Ltd.

The following elements have significant activities even a year after the concretes were exposed for neutron radiation: Ce, Co, rocks and which have a density greater than 2.9 g/cm³ (e.g. olivine, magnetite, amphibole, rutile, topaz, zircon) which are accessory constituents (<5%, but usually <0.1-0.01%) of the Cs, Eu, Fe, Hf, Sb, Sc, Ta, Tb, Cr, Pa, Sm, Sr, Zn, Th and U. All these trace elements are enriched in so-called heavy minerals performed at MTA EK, while X-ray fluorescence (XRF) measurements were done at SZIKKTI Laboratory Ltd.

Results

Based on the analytical and petrological results, we concluded that there are samples with remarkably lower, and also some with remarkably higher “impurity profile”, originated in different mines. All sand and gravel samples have SiO₂ content above 90 wt%. The major elements next to Si are Al, Fe, K and Na. Ca content is high in the Mid- and NW Hungarian gravels, while NE and SW samples have very low Ca content. Elemental analysis of the samples rates by particle size revealed that all element concentrations decrease with increasing particle size, except Cr, which has higher concentration in gravels than in sands. Grinding the samples with wolfram carbide mortar increases the W, La, Nd and also Co concentration of the samples. NE Hungarian gravel mines have the lowest trace element content, while samples from NW Hungary Babót, from Mid-Hungary Bugyi IX and Taksony, from SW Hungary Murakeresztúr II have lower trace element content.

Macro- and micro-scale gravel petrography of the samples proved diagnostic differences among the analysed three regions. It can be stated that the major rock types (and especially quartzite) are of metamorphic origin in all the observed regions. In the Mid-Danubian Region gravels have relative more igneous components compared to sedimentary ones, while in the NW Hungarian Region the gravels are more enriched in sedimentary component beside the metamorphic one. In the NE Hungarian Region gravels the cumulative ratio of igneous and sedimentary originated rocks are low (around 10 w%, and almost equal), expressing the maturity of those sediments. Based on heavy mineral studies, the gravels of the Mid-Danubian Region contain more heavy mineral carrier components.

The mine of Babót (NW Hungarian Region) has the most mature sediment formation, also indicated by high Si content at the expense of depleted other major and trace elements. Considering the radiation sensitivity, it can be stated that none of the long-lived radionuclides is enriched in the investigated sand and gravel samples compared to average Portland cement composition. However, Fe (0.5-1.5 wt%) and Cr, Sr (few hundred µg/g) show slightly higher concentrations, but all have half-lives less than a year. Cs, Co and Eu with years long half-lives are under 5 µg/g concentration in gravels. Concluding from our results, it is better to use crushed larger fractions of gravel, instead of sand to prepare low activation susceptibility shielding concrete.

Remaining work

Samples from the SW Hungarian region need to be investigated by the petrological point of view. The gravel and concrete investigation project will be carried on in the framework of V4-Korea Joint Research program between 2018 and 2022.
PREPARATION AND CHARACTERIZATION OF EFFICIENT SUPPORTED NANODISPERSED GOLD CATALYSTS


Objective
A joint bilateral project was established between the MTA EK and the Dalian Institute of Chemical Physics (DICP, China) for synthesizing and characterizing gold nanocatalysts and their use in aerobic oxidation of benzyl alcohol. The related tasks were divided between the two institutions. The preparation and characterization of \( \text{Al}_2\text{O}_3 \), \( \text{SiO}_2 \), \( \text{MgAl}_2\text{O}_4 \), \( \text{MgO} \) and hydroxyapatite (HAP) supported catalysts and a part of their catalytic investigation (in xylene solvent at 60 °C, at 1 bar \( \text{O}_2 \)) was performed at MTA EK. The other part of the catalytic evaluation (in a solvent-free condition at 150 °C, 5 bar \( \text{O}_2 \) in a sealed autoclave) was completed at DICP.

Methods
The catalyst particles were characterized with transmission electron microscopy (TEM). Adsorption and temperature programmed desorption of \( \text{CO}_2 \) and \( \text{NH}_3 \) was used for characterizing of basicity and acidity. CO adsorption was measured with two methods: i/ diffuse reflectance infrared spectroscopy, and ii/ binary concentration pulse chromatography to probe the surface gold sites. Finally, catalytic measurements with analysis of products were performed.

Results
The results of catalysis measurements on oxidation of benzyl alcohol at 60 °C, with 1 bar \( \text{O}_2 \) in xylene solvent are reported in another account in this Progress Report. Here the results of certain characterization measurements (particle size, acidity and basicity, Figs. 1 and 2) and the results of catalytic tests at 150 °C, 5 bar \( \text{O}_2 \) in solvent-free media are presented (Fig. 2).

![Figure 1: Distribution of gold particle sizes deduced from TEM images of the corresponding catalysts](image)

![Figure 2: Acidities and basicities of different supports, the conversion of benzyl alcohol at 150 °C in solvent-free media, and the yields of products after 5h reaction time](image)
The initial reaction rates in benzyl alcohol (BzOH) oxidation were determined here at 60 °C (1 bar O₂ in xylene solvent). The corresponding turnover frequencies related to surface Au atoms (TOFₚᵤᵣᶠ) ranged between 1000-4000 h⁻¹ [1]. Reactions performed in China in solvent-free media at 150 °C for 5 h resulted in a high extent of conversions. Benzaldehyde (BzO), benzoic acid (BzOOH) and benzyl benzoate (BzOOBz) products were detected with good reaction yields, amounting to 500 – 3000 h⁻¹ TOFₚᵤᵣᶠ values. Thus, the excellent performance of the synthesized and characterized catalysts is confirmed [2].

Related publications


* Dalian Institute of Chemical Physics, Chinese Academy of Sciences


APPLICABILITY EVALUATION OF ADVANCED OXIDATION PROCESS FOR ELIMINATION OF NEUROPHYSIOLOGICAL ACTIVITY ANTIDEPRESSANT FLUOXETINE

Renáta Homlok, László Szabó, Gyuri Sági, Krisztina Kovács, Szabina Papné Góger, Tünde Tóth, Erzsébet Takács, László Wojnárovits

Objective

This study aimed at seeking for an appropriate technology able to remove fluoxetine residue from a complex water matrix, where special attention needs to be paid to elimination of the neurophysiological activity [1].

Methods

For the gamma radiolysis experiments with 1600 TBq activity $^{60}$Co γ-source was used. For product analysis, liquid chromatography (LC) - tandem mass spectrometry (MS) techniques were employed. Products were separated using an Agilent 1200 LC. Density Functional Theory (DFT) was applied with the B3LYP functional using the Gaussian 09 software suite. Geometry optimizations were conducted at the B3LYP/6-311G++(d,p) level of theory, and the solvent effects of the aqueous media were considered with the Solvation Model Density (SMD) solvent model. Electronic energies were refined by single-point energy calculations using the 6-311++G(3df,3pd) basis set. Gibbs free energies were corrected for 1 M standard state of aqueous solution. For the docking studies, the virtual ligands - P4, P31, P35-37, fluoxetine and (S)-citalopram - were prepared using Schrödinger LigPrep (2016) tools applying the default settings. The physiologically relevant protonation states and tautomers were generated for both the (R)- and (S)-enantiomers using Epik. The docking calculations were carried out by Glide applying the standard precision (SP) protocol, and the rotatable groups were allowed to move.

Results

The applicability of advanced oxidation processes (AOP) to eliminate the neurophysiological activity of fluoxetine was probed by generating a free radical system with $^\cdot$OH-initiated peroxy radical mediated processes. A wide range of transformations was anticipated to occur on the fluoxetine skeleton based on product analysis experiments substantiated with computational calculations. By performing product analysis experiments along with quantum chemical calculations, the most probable reaction paths were analysed including aromatic hydroxylation, defluorination, O-dealkylation and C-dealkylation. The candidates for neurophysiological activity were further investigated by molecular docking. In the case of calculations our purpose was to differentiate between possibly active and inactive transformation products. The results of docking calculations were evaluated by analysing the interactions of the docked poses, and by comparing them with the X-ray structure of (S)-citalopram (a compound with neurophysiological activity). The (S)- and (R)-enantiomers do not show significant differences in terms of docking scores or overall layout. The docking poses were sensible for all compounds and matched to (S)-citalopram in terms of overall position. The majority of the degradation products gave scores similar to fluoxetine.

Figure 1: The proposed binding mode of fluoxetine (left) and a hydroxylated derivative (right). The ligands are shown in the middle, the hydrogen bonding side chains of the protein are on the edge of the figure, the protein itself is represented by a ribbon and the Na$^+$ ions are visualized as small spheres. The colour structures show the medicine molecules investigated.

Molecular docking studies show (Fig. 1) that the hydroxylated derivatives are well accommodated in the binding pocket of the corresponding protein, suggesting that these compounds may retain the activity of the parent compound. Therefore, we suggest that performing the AOP treatment to reach an appropriate treatment stage without hydroxylated derivatives present might be a prudent approach to handle this problem. From a worst-case perspective, we suggest that prolonged treatment needs to be applied to further transform hydroxylated derivatives.

Remaining work

The project was finished.

Related publication

Assessment of Antibacterial Activity, Toxicity and Biodegradability of Products in the Course of Radiolysis Induced Decomposition of Sulphonamides

Krisztina Kovács, Szabina Góger Papné, Renáta Homlok, Tünde Tóth, Gyuri Sági, Anna Tegze, Erzsébet Takács, László Wojnárovits

Objective

The present work is aimed at studying the removal of four sulphonamides (sulphanilamide (SAA), sulfaguanidine (SGD), sulfathiazole (STZ), sulfamethoxazole (SMX)) from their aqueous solutions by ionizing radiation with emphasis on the biological evaluation of the decomposition products. Biodegradability in river water and in activated sludge, the toxicity from three different trophic levels and the antibacterial activity were tested.

Methods

The samples were irradiated using a 60Co panoramic type γ facility (dose rate = 7.6 kGy h⁻¹) at room temperature, in aerated, 0.1 mM solutions. H₂O₂, which can form during irradiation, was eliminated by heterogeneous catalysis using 5 g L⁻¹ MnO₂ (stirred overnight at 20 °C, pH = 10). The removal efficiency was investigated by LC-MS/MS. BOD₅ experiments were performed by using an OxiTop® Control BOD Respirometer System according to DIN EN 1899-1 (1998). Activated sludge and river water were used for inoculation. The acute toxicity to the Vibrio fischeri bioluminescent bacterium (a decomposer) was determined according to DIN EN ISO 11348-2 (1999) following 30 min incubation. The chronic growth inhibition on Pseudokirchneriella subcapitata (a producer) microalgae was implemented based on OECD test No. 201 (2011) after 72 h. Daphnia magna (a consumer) acute mortality tests were performed according to OECD Test No. 202 (2004). Activated sludge inhibition tests were carried out according to ISO 8192:1986 (1986) standard over a period of 180 min. In antibacterial susceptibility testing, Pseudomonas aeruginosa was chosen as the test organism. Broth microdilution assays were carried out by photometrical monitoring of bacterial growth, employing a Multiskan Ascent device.

Results

Efficient removal of sulfonamides was achieved at 1.5 kGy absorbed dose. Readily biodegradable products can be attained at higher doses (1.5-2.5 kGy) both in river water and activated sludge. The BOD₅/COD⁻¹ ratios of the solutions in the activated sludge experiments displayed a shift to higher values as compared to results obtained in river water. There are significantly smaller amounts of bacterial species and lower microbial abundance in river water. Therefore, the low incidence of compatible enzyme producers prolonged the adaptation/acclimatization of the microbes. The ecotoxicity was dependent on both test organisms and the type of antibiotics used. Complete removal of toxic effects in the case of some sulphonamides required doses higher than 2.5 kGy at the concentration used. In respiration inhibition tests, the initial sulphonamides did not inhibit the metabolic activity of activated sludge and even co-metabolism was observed in the case of untreated SMX in the presence of a growth substrate (sodium acetate). Antibacterial activity was removed in parallel with the elimination of initial molecules. The strong correlation between concentration reduction of the parent molecule and the disappearance of antibacterial activity implies the formation of radiolytic products with no antibacterial potency in the case of SMX. [1]

Ionizing radiation treatment proved to be a suitable technique for eliminating the environmental risk of sulphonamide antibiotics. The results also showed that degradation of initial molecules is not always enough to eliminate harmful effects. For this reason, a complex biological assessment of treated solutions has to play an important role in the development and optimization of advanced treatment techniques.

Related publication

SYNTHESIS OF CELLULOSE DERIVATIVE/CLAY COMPOSITE SUPERABSORBENTS BY GAMMA-IRRADIATION

Tamás Fekete, Erzsébet Takács, László Wojnárovits, Tünde Tóth, Szabina Papné Góger

Objective
The aim of our work is the modification of the properties of cellulose derivative-based superabsorbents by the preparation of various copolymer and composite hydrogels. In the past we investigated the effect of the partial replacement of the cellulose derivative with natural or synthetic polymers. In the current work we examined the potential improvement of the gel properties by the addition of clay particles, which might allow the preparation of low-cost superabsorbents. As the composition has a large impact on the gelling behaviour, the effect of the clay component on the dependence of the gel properties on various synthesis parameters was investigated. The effect of the organic surface modification of the clay component on the gelation was also examined by using commercially available modified clays. The dependence of the gel properties on various synthesis parameters such as the absorbed dose and the solute concentration was also investigated for different clay contents.

Methods
Aqueous mixtures of different types of clay and cellulose derivatives were prepared. Hydroxyethylcellulose (HEC) and carboxymethylcellulose were used as the polymer component, while native and organically modified montmorillonite clay was chosen as the inorganic additive. \(N,N'\)-methylenebisacrylamide crosslinking agent was also added in low concentrations to improve the gelling behaviour. The crosslinking of the aqueous mixtures was carried out by gamma irradiation. The swelling behaviour and the gel fraction were determined for the prepared gels, and their morphology and chemical composition were also characterized.

Results
Cellulose derivative/clay mixtures required significantly higher solute concentrations for the gelation compared to the pure cellulose derivative solutions. While cellulose derivative/clay nanocomposites could be synthesized without the use of a crosslinking agent, not only higher dose and solute concentration was required, but relatively low swelling could be achieved for macroscopically stable gels. The gelation improved significantly in the presence of the cross linker; it allowed the use of mild synthesis conditions even in very low concentrations (0.5 w/w \(\%\) or less). The partial replacement of the cellulose derivative with natural montmorillonite clay powder led to the improvement of the swelling capacity (especially for hydroxyethylcellulose-based systems), while the increase in the gel fraction also became smaller. However, at higher clay content the gel fraction actually decreased, unless significantly higher solute concentrations were utilized. The organic modification of the clay also had an impact on the gel properties. The swelling behaviour was similar to that of the natural montmorillonite, leading to a similar gel fraction, but due to the organophilic clay surface the degree of swelling decreased. While the decrease in the swelling due to the high clay content or the surface modification of the clay may make them less suitable as superabsorbents, preliminary experiments showed that such systems may have high potential as adsorbents in the water treatment (Figure 1).

Figure 1: Comparison of the adsorption of toluidine blue dye from an aqueous solution by cellulose-based hydrogels: (a) no hydrogel, (b) pure HEC and (c) HEC/Montmorillonite composite hydrogel

Remaining work
In the future the potential application of the prepared composite superabsorbents needs to be investigated in depth, especially regarding their use as adsorbents, such as the determination of the adsorption isotherms and the effect of the clay type on the adsorption efficiency for different types of pollutants.

Related publication
V. NUCLEAR ANALYSIS AND CHEMISTRY
COORDINATED RESEARCH PROJECT ON PHOTONUCLEAR DATA AND PHOTON STRENGTH FUNCTIONS

Tamás Belgya and László Szentmiklősi

Objective

The main goals of this IAEA Coordinated Research Project (CRP) are to update the Photonuclear Data Library (1999) and to generate a Reference Database for Photon Strength Functions (PSF).

Methods

Additional measurements to the \(^{242}\text{Pu}(n,\gamma)^{243}\text{Pu}\) reaction to subtract background from the target backing of Al and the Ti layer covering the Pu target. Analysis and unfolding of \(^{243}\text{Pu},^{73}\text{Ge}\) and \(^{74}\text{Ge}\) spectra. Modelling of \(\gamma\)-ray spectra with a Photon Strength Function (PSF) calculated using the Quasiparticle Random Phase Approximation and Nuclear Level Density (NLD) data.

Results

Using an internal calibration, the spectra of partial gamma-ray production cross sections were obtained. Then, with the energy weighted sum rule, \(\sigma_0 = \sum \frac{b}{E_i} \sigma_{\gamma,i}/b_n\), the thermal capture cross section \(\sigma_0\) was determined for the target nucleus. Here, \(b_n\) is the binding energy of the daughter nucleus, \(E_i\) is the gamma-ray energy and \(\sigma_{\gamma,i}\) is the partial \(\gamma\)-ray production cross section. The \(\gamma\)-multiplicity \(M\) was calculated by dividing the sum of the partial cross sections by \(\sigma_0\). In Table 1, the experimental capture cross section and multiplicity values are given, which are important indicators of the model validity.

<table>
<thead>
<tr>
<th>Target</th>
<th>(\sigma_0) (b) this work</th>
<th>(\sigma_0) (b) literature</th>
<th>Daughter</th>
<th>Multiplicity this work</th>
</tr>
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<td>(^{72}\text{Ge})</td>
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<td>0.9(1)</td>
<td>(^{73}\text{Ge})</td>
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</tr>
<tr>
<td>(^{73}\text{Ge})</td>
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<td>(^{77}\text{Se})</td>
<td>36(4)</td>
<td>42(4)</td>
<td>(^{78}\text{Se})</td>
<td>3.6(2)</td>
</tr>
<tr>
<td>(^{113}\text{Cd})</td>
<td>21660(360)</td>
<td>26015(400)</td>
<td>(^{114}\text{Cd})</td>
<td>4.1(1)</td>
</tr>
<tr>
<td>(^{242}\text{Pu})</td>
<td>18.2(6)</td>
<td>18.5(5)</td>
<td>(^{243}\text{Pu})</td>
<td>3.9(4)</td>
</tr>
</tbody>
</table>

For the validation of the recommended microscopic QRPA (quasiparticle random-phase approximation), a simulation was performed with the BITS (Bin Type Statistical simulation) program to describe the low-lying decay-scheme intensities and the decay gamma-ray spectra. The input level density data table were obtained from Stephan Goriley. The agreement between the simulation based on the QRPA model and the experimental spectra are rather good.

In cases where two possible capture spins can be excited, the contribution weights can be obtained from the evaluated capture cross section from the EXFOR database. Adding them up by weighting with these values gives the final result. For example, in the case of \(^{113}\text{Cd}\) neutron capture mainly influenced by the first strong \(1^+\) resonance makes an almost 100% contribution to the capture cross section. This we see from the almost complete agreement of the calculated and experimental running sum of decay probabilities for the \(1^+\) capture, while for \(0^+\) it is not agreeing [1].

![Figure 1: The calculated and measured cumulative sum of decay probability for pure \(1^+\) (left) and \(0^+\) (right) capture states in \(^{114}\text{Cd}\). The calculated multiplicity is \(M = 4.02\) (left) and \(M = 3.66\) (right).](image)

Remaining work

Preparing publications on modelling of unfolded radiative neutron capture spectra.

Related publication

STABILITY OF ALL-INORGANIC PEROVSKITE NANOCRYSTALS

Dániel P. Szekrényes, Szilárd Pothorszky, Dániel Zámbó, Dávid Srankó, Ferenc Somodi, Andrea Beck, György Sáfrán, András Deák

Objective

Although all-inorganic perovskite ionic nanocrystals (e.g. CsPbBr$_3$, as used in the present work) have promising optical properties, they suffer from instability issues related to the dynamic nature of stabilizing ligand shells. This is in contrast to classical quantum dot systems, where stable particle cores and covalently attached ligands provide sufficient long-term stability for advanced applications. The aim of the current research is to investigate the stability of the all-inorganic nanocrystals from the colloid chemical and optical points of view, using (i) modification of the ligand shell and (ii) incorporation into polymer matrices.

Methods

CsPbBr$_3$ nanoparticles have been prepared based on literature protocols. During the co-precipitation of the Cs- and Pb-oleate precursors in toluene with tetraoctylammonium bromide (TOAB), vortex mixing was used to obtain nanoparticle sols typically on the ml scale. Two main approaches have been used to improve nanoparticle stability: stabilization of the particle’s surface by introducing inorganic-organic ion pairs and incorporation of the nanoparticles in optically inert polymer films (polystyrene and Zeonor®). The former was achieved by phase transferring sulphur ions from an aqueous Na$_2$S solution into toluene using TOAB. The latter was performed by spin-coating the mixture of nanoparticles and the respective polymer solution on glass substrates. The samples were characterized using dynamic light scattering (DLS – Malvern Zetasizer NanoZS), transmission electron microscopy (300kV JEOL JEM 3010) and a laboratory-built photoluminescence (PL) spectrometer ($\lambda_{exc}$=443±6 nm; filtered from a 150W Xe-lamp, detector: Thorlabs fibre coupled spectrometer).

Results

The nanoparticle synthesis has been scaled up to produce a few tens of millilitres which contains mainly nanoplatelets of 4-unit cell thickness (Fig.1a). The emission properties of the as-prepared nanoparticles could be tuned by introducing various amounts of iodide ions (Fig. 1b). Besides the successful emission tuning, the colloidal stability of the system was reduced strongly, and the particles precipitated with a gradual loss of PL intensity. The introduction of sulphur ions has an ambiguous impact. It influences the particle size, which is slightly larger (11-12 nm) compared to the as-prepared particles (9 nm). However, it decreases the colloidal stability, leading to an increased amount of sediment upon centrifuging. Nevertheless, samples treated by S$^2$- are optically more stable. They retain their PL emission upon acetone addition, whereas as-prepared samples lose most of their PL after 1 day. The change of the emission wavelength of the particles that remained stable in solution (Fig.1c) indicates the changing quantum confinement as the particles are transformed from platelets to cubes at room temperature. The sulphur ions apparently have no significant impact on the kinetics of the process, as the points follow the same trend.

However, when the particles are embedded in a polymer matrix and the toluene solvent removed (oleic acid does not evaporate), two main differences can be observed (Fig. 1d). The emission wavelength is increasing faster compared to the solution values and its final value is also higher. Additionally, at an intermediate time (120 h) a splitting of the emission peak can be observed (see inset and the corresponding points marked by arrows). In solution, particle reshaping is competing with the partial formation of a non-fluorescent precipitate (presumably PbBr$_2$) over long time scales, which reduces the actual particle size resulting in a bluer shifted emission. In the polymer film, however, the reduced mobility of the particles and ions presumably allows for a shape transformation with no, or much lower size reduction and particle loss, resulting in (i) more redshifted emission and (ii) the simultaneous presence of several particle populations.

Remaining work

Work is currently in progress to compare the data to results obtained in the case of preparation under an inert atmosphere and to perform excitation-power dependent micro-PL measurements on the polymer embedded particles.
STRUCTURAL CHARACTERISATION AND BIOCOMPATIBILITY OF PHOSPHATE BASED GLASSES FOR BIOMEDICAL APPLICATION

Margit Fábián, Viktória Kovács Kis, Csaba Araczki, Zsolt Dallos

Objective

Biomaterials are artificial or natural materials that are used to replace lost or diseased tissue and to restore form and function. Thus, the field of biomaterials has become an imperative area, as these materials are helpful in improvement of the quality and the longevity of human life. Our work focuses on the development of phosphate glasses and aims to find out the structural properties and biocompatibility of these glasses.

Methods

Samples were prepared by melt-quench technique, from reagent grade powders (SiO₂, Na₂O, CaO, P₂O₅) melted in a Pt crucible. For the study of the short and intermediate range order neutron diffraction (ND) experiments were carried out using the neutron diffractometers at the 10 MW Budapest research reactor and at the 7C2 diffractometer in Saclay. Reverse Monte Carlo (RMC) simulation was applied to generate reliable 3-dimensional atomic configurations and to calculate the partial atomic pair correlation functions, coordination number and bond angle distributions. The glasses were analysed using Stokes Raman spectra, measured at 514.5 nm Argon ion laser on Renishaw in Via-Reflex Micro-Raman spectrometer. Nuclear Magnetic Resonance (NMR) experiments were recorded on the 600 MHz Varian NMR System installed in the Slovenian NMR Centre in Ljubljana. Bioactivity was studied in vitro using simulated body fluid (SBF). Bioactivity tests were performed at 37°C and 5% p(CO₂).

Results

Bioactive glasses have been prepared by melt-quench technique in the compositional range SiO₂(45)CaO(25)Na₂O(30-x)P₂O₅(x), x=0, 1, 3, 5; signed with S45, S45P1, S45P3, S45P5, respectively. The RMC calculation based on ND data show well-defined first neighbour distances for Si-O at 1.60 Å (Fig 1a), P-O at 1.61 Å (Fig 1b), Ca-O at 2.35(56) Å and Na-O at 2.25(56) Å distributions. The average coordination number distribution shows that Si atoms are surrounded by 4 oxygen atoms (Fig 1c). RMC calculations have revealed that for all studied glassy compositions the P atoms are 4-fold coordinated by oxygen atoms (Fig 1d). These findings suggest that the network consists of SiO₄ and PO₄ units, which are supported by the bond angle distributions. The ²⁹Si NMR spectrum of glassy Si displays a single broad resonance centred at -77, -79, -81 ppm for S45P1, S45P3 and S45P5, respectively, that corresponds to the ⁴Q Si environment, consistently with literature reports. The ³¹P NMR resonances came at 9.88, 9.15 and 8.12 ppm for S45P1, S45P3 and S45P5, respectively. These positions are specific for the P-Ca(Na) complexes, example Ca₅P₃O₁₁, Na₅P₃O₁₁, Na₅PO₄, Ca₃(PO₄)₂. From NMR data the signs of the Si-O-P connections are missing. All Raman spectra contain two strong band centred near ~635 cm⁻¹ and ~945 - 1080 cm⁻¹ that can readily be assigned to the Si-O-Si; Si-O-Na and to the [PO₄]³⁻; P₂O₇⁻, respectively. From Raman analysis we detect the presence of non-bridging silicon-oxygen groups and changes in the inter-tetrahedral Si-O-Si bond environment. The concentration of non-bridging oxygens is increasing in SiO₄ units with P₂O₅ increase, it is surprising that even 1mol% can make difference. It has been found that the intensity and the frequency of the Raman lines depend on the concentration of the alkali and alkali-earth oxides in the bioactive glass. To test the biocompatibility of the glasses, samples have been treated in SBF for different soaking times (3h, 3days, 7days, 21 days). After three hours all P containing samples exhibited a Ca and P rich layer on their surface. The hydroxyapatite layer was detected, which supports the biocompatibility of the glasses.

Remaining work

Characterization of the bioactive layer as a function of composition and soaking time in comparison to the bone mineral component. The synchrotron X-ray diffraction measurements are under evaluation.

Related publications

[1] M. Fábián, V.K. Kis: Neutron diffraction and Raman spectroscopic study of bioactive silica based glasses, American Neutron Scattering Conference, lecture, 24-28 June, 2018, Maryland, USA
APPLICATIONS OF NUCLEAR ANALYTICAL TECHNIQUES

Zsolt Kasztovszky, László Szentmiklósi, Boglárka Maróti, Ildikó Harsányi, Zoltán Kis, Veronika Szilágyi, Katalin Gméling

Objective
Elemental composition measurement using prompt-gamma activation analysis (PGAA) and instrumental neutron activation analysis (NAA). The compositional data measured here are easily applicable to catalysis, material science, geochemistry and heritage science. The access of non-Hungarian users to the instruments has been supported by transnational access programs, including CERIC-ERIC and H2020 IPERION CH.

Methods
PGAA with cold neutrons has been applied in combination with NAA and portable X-ray fluorescence analysis (XRF) to measure major, minor and trace components of the samples, benefiting from the complementarities of these methods.

Results

Heritage Science (Archaeometry)

- The compositions of polished stone axes made from metamorphic rocks have been measured: a set of nephrite, serpentine, metabasalt, blueschist, etc. archaeological and geological samples have been analysed. The objects were obtained from Hungarian museums, and from international collaborations, whereas the raw materials have been collected by fieldwork. The aim of the study is to identify the origin of the raw materials (i.e. the provenance of the objects). With the help of the PGAA method, certain rocks have been classified more precisely, and the possible places of origin of raw materials have been confined to a well-defined region. Three manuscripts have been published to summarize the results about stone tools made of high pressure metamorphic rocks [1, 2, 3]. An overview publication was also published about the applicability of the neutron techniques in the provenance research of archaeological stone objects [4].

- In collaboration with domestic user groups (Lendület, OTKA, “Bakota”), different historical bronze objects, such as axes, a spearhead, and decorative spirals were analysed by PGAA and pXRF to determine their chemical compositions [5]. Additional information was obtained using neutron radiography. Based on the results (e.g. the Sn, As and Ni content), conclusions regarding the production technique could be drawn.

- By far the most valuable cultural object that has been analysed by neutron methods at BNC is a bronze sculpture “The Budapest Horse and Rider” attributed to Leonardo da Vinci. The aim of the PGAA in this study was to confirm if the rider, the horse and its tail were cast with the same technique from the same raw material, and to determine the composition of the filling material identified earlier by non-invasive imaging. The various pieces of evidence point towards the conclusion that the sculpture was indeed made by da Vinci. The sculpture became the highlight of the re-opening ceremony at the recently renovated Museum of Fine Arts [6].

- A promotion video was made available on-line about the cultural-related activities of the Laboratory. A case study on a bronze spearhead of the Hungarian National Museum was presented and the synergetic use of multiple techniques was demonstrated [7].

Geology and Environmental research

- Our laboratory, with PGAA and NAA measurements, took part in the IAEA organized inter-laboratory comparison studies of WEPAL (i.e. Wageningen Evaluating Programs for Analytical Laboratories), soil (ISE - International Soil-Analytical Exchange) and plant (IPE - International Plant-Analytical Exchange) samples with excellent results in the comparison to the reference data and to the results of other participating laboratories [8]. The NAA-PGAA e-learning tool is also being upgraded with the involvement of our staff members.

- A pilot study on 3 fossilized echinoids (sea urchins from the Middle Miocene) has been done at the NIPS-NORMA station. Neutron tomography, as well as bulk PGAA of a restricted volume within the investigated specimens is expected to provide compositional information both on the calcium carbonate shell and the inner part (stomach, divided into five parts) of the sea urchins. Such information could help ecologists and marine biologists to reconstruct the ancient palaeo-environment. 3D structure light scanning was also accomplished to accurately determine their dimensions and provide photorealistic appearance of the dataset obtained by neutron tomography.

Chemistry and Material science

- Alkane oxyhalogenation attracts increasing attention as an alternative route for natural gas upgrading. Operando prompt gamma activation analysis, which correlated catalyst performance and surface halogen uptake, was applied along with of operando photoelectron photo ion coincidence spectroscopy and density functional theory. We have found that ethyl halide generation occurs on the catalyst surface in oxychlorination, while it primarily follows a gas-phase
radical-chain mechanism in oxybromination. Finally, dehydrohalogenation of the ethyl halide intermediate was favoured on a chlorinated surface, while in oxybromination, Br• radicals evolution led to polybromination, rationalizing the mechanistic difference that results in the observed selectivity trends [9].

**Remaining work**

We will continue the applications of PGAA and NAA in thematic research projects and also in international TNA (Technology needs assessment) projects (IPERION CH, C-ERIC).

**Related publications**


DEVELOPMENT OF NUCLEAR ANALYTICAL TECHNIQUES, NUCLEAR DATA MEASUREMENTS & DISSEMINATION ACTIVITIES

László Szentmiklósi, Boglárka Maróti, Zoltán Kis, Tamás Belgya

Objective
To develop our analytical capabilities and know-how in Prompt-Gamma Activation Analysis (PGAA) and Imaging (PGAI), to accurately determine related nuclear data, and to provide training and education for guest researchers and students.

Methods
The methods used were \((n,\gamma)\) measurements, PGAA, PGAI-NT, evaluation of nuclear data and comparison to literature, computer programming, Monte Carlo modelling, teaching.

Results
Within the framework of the OTKA Grant No. K124068 project we developed the Monte Carlo models of the PGAA and NIPS experimental setups using the recently released software package MCNP 6.2. The \textit{geant4} implementation of the PGAA station is complete, while that for NIPS-NORMA is in progress. The ENDF/B-VIII.0 nuclear data library was used within both programs to avoid the bias due to differences in input parameters. The performances of the two software packages are being evaluated for prompt-gamma spectrometry as well as for neutron imaging.

Figure 1: The MCNP 6.2/\textit{geant4} models of the Budapest PGAA facility

We worked out two approaches, the voxel-wise 3D discretization, and the mesh-based geometry approach, to load sample geometries to the simulation environments. Voxel data can be directly taken from tomography after proper pixel binning, while the 3D meshes could be obtained either using a RangeVision SMART 3D structured-light scanner or from the advanced surface determination algorithm applied on segmented neutron/X-ray tomography data using the VG Studio MAX software.

Figure 2: Photorealistic 3D-scanned model, and the MCNP 6.2/\textit{geant4} representations of a gray flint stone sample

Simulations for self-attenuation and self-absorption beyond the present state-of-the-art are being developed to improve our analysis capabilities for irregularly shaped or structured objects. Experiments were carried out with the cold and thermal (polychromatic) neutron beams at PGAA to measure the neutron and gamma attenuation of layered structures. Combinations of metal foil pairs, as well as 3D assemblies of 7-mm unit cubes made of Cu, Sn, Fe, Pb, PTFE, and clay were used in the experiments to form the dataset to validate the Monte Carlo calculations. The X-ray emission spectrum of our X-ray generator was estimated with the SpekCalc software.

Using 3D additive manufacturing technology (a.k.a. 3-D printing), plastic replicas of complex-shaped objects as well as ad-hoc sample holders were fabricated [1,2], in collaboration with J. Janik, Reactor Department.
The analytical merits of PGAA, in-beam NAA, reactor-NAA and handheld XRF were compared on bronze alloys. A recommended analytical workflow was established to non-destructively characterize these alloys [3]. Neutron imaging was shown to be essential in the analysis of heterogeneous samples to complement the surface and bulk analytical results with 3D visual information. The conclusions were included in a PhD dissertation, which has been defended at the Hevesy György PhD School of Chemistry of the Eötvös Loránd University [4].

Data from two of last year’s nuclear physics experiments were processed and papers were submitted for publication. To search for the bound deuteron singlet state, a radiative neutron capture experiment on hydrogen was made. The existence of the bound state singlet deuteron might have been evidenced by a two-step gamma-ray transition at about ~ 100 keV below the primary gamma ray energy of 2223 keV. Even from a long measurement, we found no evidence for the two-photon transition in the region 2100-2210 keV, so an upper limit in the branching ratio $\sigma < 2\mu$b (two standard deviations uncertainty) was set, being an order of magnitude less than earlier measurements indicated.

Partial gamma-ray production cross sections from thermal neutron-capture were measured for the $^{139}\text{La}(n,\gamma)$ reaction with a thick and a thin $^{208}\text{La}_2\text{O}_3$ target [6]. Here we successfully assessed the self-absorption difference of the two targets using the equivalent thickness approach. Absolute $^{140}\text{La}$ cross sections were determined relative to the well-known comparator $^{35}\text{Cl}(n,\gamma)$ cross sections from the irradiation of a stoichiometric $^{35}\text{Cl}_3$ sample. The total cross section for radiative thermal neutron-capture on $^{139}\text{La}$ was determined to be 8.58 (50) barns from the sum of experimentally measured cross sections observed to directly feed the $^{140}\text{La}$ ground state.

Education and dissemination activities

- The neutron-energy-distribution of the RAD facility was determined, based on the activation-foil approach, with the involvement of a summer-student, Guilhem Paradol, from Univ. of Grenoble, France (mentored by T. Belgya).
- A PhD course at Eötvös University, ‘Nuclear Analytical Methods and their Application in Earth Sciences and Archaeometry I-II.’ was taught.
- Lectures and hands-on training at the Central European Training School on Neutron Techniques 2018
- PGAA laboratory training for BME and ELTE students

Related publications

VALENCY STATES OF IRON AS PROBED BY MÖSSBAUER SPECTROSCOPY

Károly Lázár, Sándor Stichleutner, Zoltán Klencsár

Objective

Iron is an important constituent in various systems and identification of its valency (Fe$^{3+}$, Fe$^{2+}$ or Fe$^{0}$) is essential for interpreting the observed properties. Recently, iron-based magnetic silica/polymer nanocomposites used for targeted drug delivery and conversions of different iron compounds in a process applied for separate recovery of Zn and Fe from ZnFe$_2$O$_4$ galvanization sludge as well as formation and stabilization of various iron alloys and compounds during electric explosion of wires in various liquid media were studied.

Methods

$^{57}$Fe transmission Mössbauer spectroscopy was applied principally, amended with other appropriate techniques.

Results

Magnetic dual drug delivery system was developed for targeted combined administration of anticancer mitoxantrone and anti-inflammatory prednisolone. 100 nm mesoporous silica globules were grown around 10 nm maghemite nucleation cores, and were functionalized with appropriate compounds. Mössbauer spectroscopy revealed the dominance of Fe$^{3+}$ state and maghemite structure in the cores of nanoparticles [1].

$\text{(NH}_4\text{)}_2\text{Fe(SO}_4\text{)}_2\cdot6\text{H}_2\text{O}$ (Mohr’s salt) and $\text{NH}_4\text{Fe(SO}_4\text{)}_2\cdot12\text{H}_2\text{O}$ were applied to accomplish separate recovery of iron and zinc from the ZnFe$_2$O$_4$ component of galvanization sludge. It was demonstrated that the sulphation reaction with ammonium iron sulphates could be performed at lower temperatures than with other iron sulphates used conventionally. Various reaction intermediates were identified by Mössbauer spectroscopy providing means to interpret the conversion processes [2].

Method of electric explosion of wires (EEW) was applied to produce nanoparticles from iron and ASI-304 steel as well as from Kovar alloy wires in various liquid media (water, paraffin oil, ethylene glycol, siloxane). Metallic globules were obtained principally in various size distributions, as expected. However, wide variety of products was also identified which were condensed from reactions of vaporized components formed from both the metal wire and the decomposed liquid medium in a short life-time plasma of the discharge process [3]. Mössbauer spectra provided an appropriate tool to analyse the various the various products (Figure 1).

Related publications


Radiotherapy and Tomography at BRR

Zoltán Kis, László Horváth, László Szentmiklósi

Objective
To develop and apply imaging instrumentation and methodology at the Budapest Research Reactor (BRR).

Methods
The development and application of fast neutron sensitive screens have been being continued in collaboration with the PSI (Paul Scherrer Inst.), Switzerland and Pennsylvania State University, US. A systematic investigation of casting defects for objects and the systematic study of porous materials (geology, paleontology, ceramics) were carried out by evaluating tomographic datasets.

Results
Simple and inexpensive ZnS-based fast neutron imaging screens have been developed, and their performance has been compared to a commercially available one at RAD station. The in-house screen produces about 60% of light intensity of the commercial polypropylene/ZnS screen (Fig.1a), which is mainly due to the lower hydrogen density of the optical epoxy compared to polypropylene by the same amount. A spatial resolution of around 1.6 mm has been achieved (Fig.1b). Fast neutron tomography was applied to image an energy storage and power generation system for planetary exploration missions with lithium metal as fuel. We measured a 1/3 volume ratio for each burnt, partly burnt and unburnt region. The results have great value for improving and optimizing the future oxidizers. The casting defects of a heatsink made of aluminum alloy were detected as shown in Fig.1d. The overall porosity is 0.21%, however, the largest voids are concentrated in a relatively small volume pointing a likely fatigue during the lifetime of the piece. In a pilot study, in cooperation with Wismar University, 3D imaging of the moisture-dependent spread of injection agents (synthetic resins) in bricks was evaluated. Such knowledge should be used to mitigate damages of mostly historical buildings because there are no legal standards how to realize functional sealing. In Fig.1e one can see the planar cuts of the bricks after injection showing the spatial distribution of the agent. A clear dependence on the moisture level (90%, 70% and 50%, from right to left) could be detected, and the distribution was compared against the untreated sample (most left). It could be seen that the injection process had a problem in the case of the 70% moisture level. Again, a pilot study was accomplished for the detection of the salt transport by non-destructive neutron methods in building materials. Desalination using poultices relies on the principle that salts dissolved in water are transported from the salt-contaminated, porous, mineral building materials into the poultice. The process of salt transport between a salt-loaded (NaCl) substrate and the poultice was followed by neutron radiography driven PGAI (Prompt-gamma Activation Imaging) measurements. In Fig.1f one can see the temporal behavior of the Cl concentration (upper three curves: poultice, lower five curves: stone) in a four days period.

Related publications
PREPARATION AND STUDIES OF POLYSACCHARIDE DERIVATIVE-BASED NANOSTRUCTURES

Tünde Tóth, Sándor Kurunczi, Tamás Fekete, Róbert Horváth

Objective

The aim of our work is to develop superabsorbent nanofibers made from natural resources, namely polysaccharides and their derivatives. Most of the practically applied superabsorbents (acrylate-based gels being the most widely used) are non-biodegradable. Therefore, producing gels with high water uptake made from renewable and biodegradable materials is of great practical importance. Such a renewable source is cellulose, the most abundant renewable material on earth, which can also be easily functionalized for absorption due to its hydroxyl groups. The basic steps we wish to develop are the electrospinning of cellulose derivatives from an aqueous solution using different spinning parameters, the irradiation of the nanofibers for initiating crosslinking by different doses, and the analysis of the products. Another field of our activity is the development of carboxymethyl-dextran (CMD) layers for biosensors and cell adhesion experiments. We focused here on the surface structure of the CMD thin layers and their mechanical characterization by an Atomic force microscope (AFM).

Methods

The materials used are cellulose based polymers, hydroxyethyl-cellulose (HEC) and carboxymethyl-cellulose (CMC). Both types are strong gel forming materials which could be utilized as superabsorbents after crosslinking. Two types of HEC with different molecular weight (720k and 1300k Da) and one type of CMC (700k Da) were used. Analytical quality, multiple-distilled water was used as the solvent, occasionally in combination with isopropyl alcohol. The electrospinning setup consisted of three primary components, a high voltage power supply, a pump and syringe with a metallic needle, and a grounded collector. The resulting nanofibers were investigated with a scanning electron microscope (SEM). The nanostructure of the CMD layers has been studied by a Nanosurf Flex AFM system.

Results

The solution concentration of CMC 700 was not high enough for generating the entanglements of macromolecules which is necessary for fibre formation. Since the viscosity of more concentrated solutions was too high for electrospinning, the experiments with CMC 700 were suspended. In the case of HEC 720 and HEC 1300, different spinning parameters were tried (concentration of solution, voltage, needle-collector distance, see Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (w/w %)</th>
<th>Voltage (kV)</th>
<th>Spinneret-collector distance (cm)</th>
<th>Sample</th>
<th>Concentration (w/w %)</th>
<th>Voltage (kV)</th>
<th>Spinneret-collector distance (cm)</th>
</tr>
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<tr>
<td>HEC 720</td>
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<td>20</td>
<td>12</td>
<td>HEC 1300</td>
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<tr>
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<td>12</td>
<td>HEC 1300</td>
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<tr>
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<td>20</td>
<td>22</td>
<td>HEC 1300</td>
<td>1,5</td>
<td>37,5</td>
<td>25</td>
</tr>
<tr>
<td>HEC 720</td>
<td>1,6</td>
<td>30</td>
<td>22</td>
<td>HEC 1300</td>
<td>2</td>
<td>35</td>
<td>25</td>
</tr>
</tbody>
</table>

Solutions of HEC 1300 with a water-isopropyl alcohol solvent mixture (water/isopropyl alcohol ratios were 1:3 and 3:7) were prepared and tested in the electrospinning process. Although during electrospinning it looked like the experiments were successful. SEM investigation showed that electrospaying occurred instead of fibre formation. No fibres, but only small droplets and particles reached the collector, forming spheres with diameters of 1-2 µm.

In the biosensor and cell adhesion work, the AFM revealed a homogeneous, smooth surface of CMD layers as prepared by our spin-coating method. The mechanical characterization of these layers (force spectroscopy) showed stiff layers in the dried state, while these dextran layers become fully hydrated in aqueous solution and soft. These soft CMD layers will be used in cell adhesion studies.

Remaining work

We wish extend the studies with other polysaccharides, characterizing the nanofibers, and finding new materials for the production of crosslinkages in polymers.
VI. RESEARCH AND DEVELOPMENT IN INSTITUTE OF TECHNICAL PHYSICS AND MATERIAL SCIENCES
A NEW GENERATION ELECTRON MICROSCOPE FOR THE OPEN LABORATORY OF THE HUNGARIAN MATERIALS SCIENCE

(VEKOP-2.3.3-15-2016-00002)

Béla Pécz, János Lábár

A new laboratory with the first spherical aberration corrected TEM/STEM in Hungary was opened on 11th of June 2018 in our Institute. The work started years earlier, when members of the Thin Film Physics Department took study trips to different laboratories in order to learn the technique. The first proposal was submitted to NKFIH in 2016, then with their specific support a second step proposal to our Ministry of Economy. It was a continuous work for two years to get the support, select the appropriate model and carry out a very rigid public procurement procedure. Finally, a Thermo Fisher Scientific FEI THEMS 200 model was selected with an image corrector. The preparation of the appropriate room started with moving an old microscope to another room, as the group wanted to keep and run the existing 200 kV analytical and the 300 kV high resolution (equipped with an EELS (Electron Energy Loss Spectroscopy)) microscopes beside the new one. A far more sophisticated installation environment with a very stable, precise temperature controlled air condition and stray magnetic field cancel system was constructed.

The onsite tests after installation exceeded our expectations and the factory guaranteed parameters. Factory stated TEM resolution at 200 kV is 0.09 nm, i.e. 90 pm. The tests show that a resolution of 70 pm is attainable.

The microscope can be operated at 80 kV still having a very good resolution thanks to the spherical aberration corrector. Sensitive materials including 2D layers can be investigated at that low voltage operation.

The analytical measurements in the new microscope are provided by the SuperX system comprised of 4 EDS detectors built into the column. There is no need to tilt the sample in order to get a good signal to noise ratio.

In the following we will show some examples proving the superior capability of the microscope.

Figure 2: The image shows a small gold particle at atomic resolution. As the spherical aberration \( C_s \) is intentionally set to a very small negative value, the atoms appear with bright contrast on the image.

Figure 3: Diamond lattice imaged in TEM mode revealing the diamond dumbbells with the distance of 89 pm, (400) lattice spacing in diamond. This is a very important demonstration of the resolution power. In the case we do not have the resolution below 90 pm these two close dots (i.e. two rows of carbon atoms) are imaged as one intensity spot in the high resolution image.
Figure 4: Graphene foil in high resolution imaged at 80 kV

Figure 5: Although this is not a probe corrected microscope the power of the EDS mapping can be demonstrated on a SrTiO$_3$ thin specimen in which the Ti and Sr atoms can be distinguished.

Figure 6: The above images are taken in STEM mode. The left one is an HAADF (High-angle annular dark-field) image showing gold grains with high intensity, as the brightness is monotonically increasing with the atomic number ($Z^2$). This itself makes possible to map the details of any specimen in which we can observe variations of $Z$. However, the right side image is a spectrum image taken on the same area of the sample (Au/GaAs sample ion beam mixed and annealed) We can observe not only gold crystallites (in the reality they contain already some gallium therefore the colour in the EDS map is darker than the yellow colour of gold) is embedded into GaAs, but a thin GaAs on the top of the sample as well. The results were presented at the Workshop dedicated to the 85$^{th}$ birthday of Prof. J. Gyulai.

The new contrast mechanism of the corrected TEM, namely imaging with negative $C_w$ facilitated the identification of the crystallographic phase of a precipitate by comparing the experimental image to the simulated images of the possible phases. An Al-alloy with low (0.14wt%) Zr-content contained spherical precipitates embedded in the Al-matrix. EDS analysis showed that the precipitate contains Zr and Al, but the elemental ratio could not be determined due to the undefined contribution of the surrounding, encapsulating Al-matrix. Two phases appeared in the literature to describe such spherical Al-Zr precipitates, both with identical cubic crystal structure. The difference between the two is that in the first, Al atoms sit at the corners of the cube and Zr atoms at the centres of all faces and in the second their positions (and so the proportion of the elements) are reversed. We recorded an experimental image with negative $C_w$ from a region that contained such a precipitate of 12 nm diameter, together with the surrounding matrix. Simulated images were also calculated for both phases and for the Al-matrix.
Figure 7: A magnified, selected region of the above image shows (below) the transition from the Al-matrix to the precipitate. There is serious overlap between the matrix and the precipitate in the transitional region. Atomic columns are bright with negative C. Structural features with the same size are marked with blue in the matrix, in the transitional region and in the precipitate.

Figure 8: The projected potentials were calculated with the JEMS program for the [111] direction of all three structures. The same structural features are also marked in the simulated images.

It can be seen that on the one hand there is perfect match between measured and simulated images for the matrix. On the other hand, simulated image for phase Zr$_3$Al perfectly matches the measured one (four times bright triangles with a darker spot in the middle), while the simulated image of the other phase is completely different, making phase identification unambiguous. The precipitate is cubic Zr$_3$Al.
Single-atom catalysts have recently shifted into the spotlight of heterogeneous catalysis research. Among their major appeals are the ultimate efficiency of material utilization and the simple and well-defined nature of the active centres, holding the promise of rational catalyst design. The major challenges are the preparation of a high density of firmly bound individual single-atomic centres, as well as establishing reliable structure-activity relationships. Both platinum group and transition metal atoms were found to be catalytically active in single-atomic form. Embedded in the proper matrix, also non-metal atoms can become catalytically active centres. We demonstrate that 2D crystals can provide an efficient template for realizing single-hetero-atom catalysts with a high density of non-metal single-atomic active sites. Such single-atom catalysts obtained through substitutional doping of 2D MoS$_2$ crystals with oxygen can provide the advantages of an easy and versatile synthesis, a supreme site density, and a well-controlled and characterized active site structure.

By means of atomic resolution STM investigations we were able to image a novel oxidation reaction of the MoS$_2$ single-layers at single-atom level, providing unexpected insights. In contrast to the generally accepted view, our results clearly evidence that the basal plane of 2D MoS$_2$ crystals spontaneously oxidized upon long-term ambient exposure. Instead of O chemisorption or full conversion to MoO$_3$, a novel oxygen substitution mechanism has been revealed, where individual S atoms of the basal plane are one by one replaced by oxygen atoms giving rise to a new 2D MoS$_{2-x}$O$_x$ solid solution crystal. As MoS$_2$ single layers are the most widely investigated 2D materials besides graphene, the ability to chemically modify their single atomic sites provides a novel strategy for highly efficient defect engineering as well as synthesizing novel 2D crystals with tuneable chemical compositions.
Most importantly, we have observed a significantly enhanced catalytic activity for hydrogen evolution of 2D MoS$_2$-O$_x$ as compared to its pure 2D MoS$_2$ form. We have shown that the individual O atom dopants are responsible for significantly increasing the catalytic activity. The Tafel slope for MoS$_2$-O$_x$ crystals was decreased to 67 mV dec$^{-1}$ as compared to pristine MoS$_2$ (98 mV dec$^{-1}$) and approached that of the Pt (54 mV dec$^{-1}$). Introducing the electronegative O atoms generates sites with higher electron affinity (~0.88 e$^-$), which gives rise to localized negative charges attracting H$^+$ to participate in reductive coupling to form H$_2$. Consequently, 2D MoS$_2$-O$_x$ crystals emerge as highly efficient, non-precious, earth-abundant catalysts for H$_2$ evolution with a high density of single-atomic active sites on their basal plane. Upon optimization, such catalysts hold the potential to closely approach the catalytic activity of platinum at much lower costs.

Synthesizing single atom catalysts with well dispersed identical active centres is highly challenging. Even today, the relatively low site density is a major limiting factor for the activity of single atom catalysts, as the stable anchoring (strong bonding) of individual heteroatoms to substrates is required for preventing their aggregation. Our results evidence that 2D transition metal chalcogenides can provide ideal substrates for the stable anchoring of various heteroatoms, through substituting single atoms from the host crystal lattice with various heteroatoms. These findings open the way towards developing non-metal single atom catalysts by using transition metal chalcogenide single-layers as an active substrate, opening new perspectives in single atom catalysis.
Direct-indirect bandgap and semiconductor-metal transitions in MoS$_2$ single-layers at moderate strain

(ERC StG, Korea-Hungary Joint Laboratory, Lendület)

J. Pető, P. Vancsó, G. Dobrik, P. Nemes-Incze, G. Kukucska (ELTE), J. Koltai (ELTE), L. Tapasztó

Strain-engineering the properties of 2D MoS$_2$ crystals has been intensely investigated for the last couple of years. Tuning the band structure by applying mechanical strain can provide an efficient way to fit the properties of the material to the specific requirements of various electronic and opto-electronic applications. Theoretical studies predict a steady decrease of the bandgap upon increasing of uni- and biaxial strain. Furthermore, it is expected that increasing the strain leads to a direct-indirect bandgap transition that was predicted to occur between 0.47 – 2.7% strain depending on the theoretical model, while increasing the strain up to about 10% is predicted to give rise to a semiconductor-metal transition. Photoluminescence (PL) measurements confirmed that tensile strain can reduce the optical bandgap of 2D MoS$_2$ crystals. However, the experimental demonstration of the direct-indirect gap and semiconductor-metal transitions remained challenging.

Here we study MoS$_2$ nanobubbles emerging at the interface of MoS$_2$ single layers with Au(111) substrate. Such bubbles are shown to induce a few percent of biaxial tensile strain in the MoS$_2$ lattice. We employed Raman spectroscopy to determine the amount of strain in MoS$_2$ nanobubbles, and scanning tunneling microscopy (STM) and spectroscopy investigations to directly measure the fundamental bandgap of the strained MoS$_2$ monolayers.

Figure 1: Nanobubble formation at the MoS$_2$/Au(111) interface. a) STM image revealing the presence of several nanoscale MoS$_2$ bubbles. b) 3D STM image of an individual MoS$_2$ nanobubble.

In order to experimentally determine the amount of mechanical strain induced in the MoS$_2$ lattice in the bubble areas, we performed confocal Raman spectroscopy measurements and calculations. The best agreement was found when considering 2% of bi-axial tensile strain.

By tunneling spectroscopy on MoS$_2$ nanobubbles, we were able to measure the fundamental bandgap of MoS$_2$ single layers subjected to 2% of biaxial tensile strain. We found that this strain decreases the bandgap of 1.4 ± 0.15 eV below the 1.7 eV optical gap, evidencing that the direct to indirect bandgap transition has already occurred at 2% tensile strain, in good agreement with DFT calculations. Furthermore, the combination of a few percent of tensile strain with the intrinsic n doping of the MoS$_2$ layers can provide a metallic character to MoS$_2$ single-layers already starting from modest strain values (2-3%).
To understand the mechanism of the strain-induced changes in the band structure, we have performed DFT calculations. These calculations show that at 2% of tensile strain the bandgap is reduced by about 0.46 eV, and becomes an indirect gap between the K and Γ points of the Brillouin-zone, in good agreement with our experiments. Furthermore, the calculations evidence that the bandgap reduction is almost entirely due to the downshift of the conduction band, again in excellent agreement with our experimental observation (Fig 2b).

These findings experimentally demonstrate a particularly efficient strain-engineering of the fundamental gap, which can be exploited in electronic applications, for example, by strain patterning type I heterojunctions. Furthermore, our results also clearly reveal the limitations of the strain-engineering approach. The direct-indirect transition restricts the opto-electronic applications, while the semiconductor-metal transition puts a strong limit on electronic applications above 2% of strain, where the 2D MoS$_2$ crystals acquire a metallic character.
MEASURING THE EDGE STATES OF Pt₂HgSe₃, A ROOM TEMPERATURE TWO-DIMENSIONAL TOPOLOGICAL INSULATOR CANDIDATE

(Lendület LP2017-9, ERC StG NanoFab2D, H2020 Graphene Flagship)

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The realization that the geometrical concept of topology has a profound influence on the band structure of solids is no doubt one of the most surprising and wide-reaching discoveries in the last decades of condensed matter research. Materials that are characterized by the $\mathbb{Z}_2$ topological invariant are insulating in the bulk and have conductive edge channels on their surfaces or edges. These edge states carry dissipationless current and could be a platform to realize topological quantum computation. A prototype of this is actually graphene, but the fact that the material is a topological insulator remains a theoretical curiosity, due to the negligible spin orbit coupling (SOC) strength of carbon. Therefore, the hunt is on for materials that have a large topologically non-trivial band gap, preferably in the room temperature regime (>77 meV).

Jacutingaite (Pt₂HgSe₃), a naturally occurring layered mineral has been recently predicted to be a topological insulator, with a band gap above room temperature. One can consider it a “heavy metal” version of graphene, with large SOC. By performing scanning tunnelling microscopy (STM) measurements on the material, we reveal the honeycomb-like configuration of the basal plane states (see Fig 1a, b). Our density functional theory (DFT) calculations predict a topologically non-trivial gap of 110 meV. This value is reproduced by tunnelling conductance measurements on the bulk basal plane. Its topological character is confirmed by calculating the $\mathbb{Z}_2$ invariant. In Fig. 1e we can observe how the density of states within the gap increases, if we move the tip of the STM closer to a monolayer step edge on the surface. This observation is expected if the topological edge state resides within the band gap. By mapping the tunnelling conductance within the gap, as a function of position, it becomes clear that the increased density of states follows the step edge, with a decay of ~5 Å into the bulk, as expected from DFT calculations (see Fig. 2).

The identification of the topological edge states makes Pt₂HgSe₃ a prime candidate for applications of 2D topological insulators, with the promise of achieving room temperature dissipationless transport, or the realization of a topological superconductor.

Figure 1: STM measurements on Pt₂HgSe₃. (a) Atomic resolution STM image of the basal plane, showing the honeycomb structure of Pt₂HgSe₃. (b) Atomic lattice of a single layer of Pt₂HgSe₃. (c) DFT calculation of its bands. Grey plot shows the bands of a single layer without spin orbit coupling. Red and blue bands are calculated with spin orbit coupling taken into account. The colour represents the contribution of Pt and Hg atoms. (d) Density of states measured on the basal plane (blue) and calculated via DFT (red). (e) Tunnelling conductance measurements nearing a monolayer edge, showing the appearance of states inside the predicted topological band gap.
Figure 2: Images of the topological edge state. (a) STM topographic image of a monolayer step edge. Tunnelling conductance images measured at the edge, at a sample voltage inside the band gap: (b) and out of the band gap in the conduction band: (c).
HIGHLY ORDERED GRAIN BOUNDARIES IN CVD MoSe₂ SINGLE LAYERS

(ERC StG NanoFab2D, Graphene Flagship)

A. A. Koós, P. Vancsó, G. Dobrik, L. P. Biró and L. Tapasztó

The chemical vapour deposition (CVD) growth method is one of the most widely investigated techniques to achieve a scalable growth of macroscopic area 2D crystals. However, CVD grown layers also suffer from a few drawbacks as compared to high quality, but microscopic exfoliated 2D transition metal dichalcogenide (TMDC) flakes. In general, CVD grown layers are expected to contain a much higher concentration of grain boundaries that are known to substantially affect their electronic and optical properties. Grain boundaries in TMDC materials are often characterized by structural disorder and a substantial local modification of the band gap that both act as source of charge carrier scattering, degrading the electronic quality of CVD grown sheets. Nevertheless, growing large area single crystalline domains is highly challenging. Even if one can drastically reduce the nucleation site density, it requires an extremely slow growth process. Consequently, growing macroscopic areas of TMDC single layers of high structural and electronic quality is a particularly important, yet unsolved challenge.

In general, grain boundaries provide a strong intrinsic limitation to the structural and electronic quality of the CVD grown single layers. Consequently, revealing their atomic and electronic structure is of particular importance. We were able to achieve atomic resolution STM images on or around several MoSe₂ grain boundaries, as shown in Figure 1. All atomic resolution STM images evidence that the atomic lattices on the two sides of a MoSe₂ grain boundary have closely matching orientations. The prevalence of this special class of grain boundaries is due to the rotationally aligned CVD growth of MoSe₂ on graphite. We found that the most often observed mirror twin boundaries (MTBs) running along the zigzag directions are highly ordered, while those enclosing an angle with the zigzag direction (but still preserving the rotational alignment of the two sides) are characterized by a more disordered atomic structure. To get insight into the electronic structure of the MoSe₂ grain boundaries, we have also performed tunnelling spectroscopy measurements on various GBs (Fig. 1c). Tunnelling spectra on disordered MTBs enclosing a nonzero angle with the zigzag crystallographic direction display a substantially reduced band gap due to emerging midgap electronic defect states. By contrast, tunnelling spectra of zigzag grain boundaries are very similar to those recorded on the defect free MoSe₂ regions, evidencing that zzMTBs do not perturb strongly the electronic properties of the crystal. To understand the electronic properties of the experimentally observed zzMTBs in more details, we have performed DFT calculations on several possible zzMTB geometries.

Figure 1: a, b) Atomic resolution STM images of mirror twin grain boundaries in CVD MoSe₂ running along various crystallographic orientations measured relative to the zigzag direction. c) Representative tunnelling spectra of various grain boundaries.

Figure 2: Calculated atomic and electronic structure of various MoSe₂ MTBs with (Se) zigzag orientation. The inset shows the simulated STM images of the corresponding atomic structures.

We have shown that in contrast to other types of grain boundaries, mirror twin boundaries running parallel to the zigzag crystallographic direction of the MoSe₂ lattice are characterized by a highly ordered atomic structure and leave the electronic structure almost unaffected; while grain boundaries with other orientations display a more disordered structure and substantially modify the band gap locally. Zigzag mirror twin boundaries do not degrade the electronic quality of CVD grown MoSe₂ single layers.
MECHANICAL STRAIN PUTS A TWIST ON DIRAC FERMIONS IN GRAPHENE

(Lendület LP2017-9, ERC StG NanoFab2D, H2020 Graphene Flagship)

P. Kun, G. Kukucska (ELTE), G. Dobrik, J. Koltai, J. Kürti (ELTE), L. P. Biró, L. Tapasztó, P. Nemes-Incze

One of the hallmark properties of graphene is that backscattering of charge carriers is prohibited for smooth potentials. This is a major characteristic of the massless Dirac quasiparticles in graphene and was recognized early on, in the very first charge transport measurements of single graphite layers. Forbidden backscattering in perfect graphene is intimately linked to the pseudospin property of Dirac fermions and lies at the heart of the exceptional electrical properties of graphene.

![Figure 1: Anomalous D' peak intensity in Raman spectroscopy measurements on crumpled graphene. (a) Pseudospin conservation and intra-valley scattering in graphene, emphasizing the process leading to the D' peak. (b) AFM image of a crumpled graphene sample, with the Raman measurement position shown by green circle. (c) Raman spectrum measured on the crumpled graphene, showing a D' peak with an intensity 300 times the D peak intensity.](image)

The “spin-like” property is a result of the crystal symmetry of graphene and determines the phase that the Dirac wavefunction acquires while scattering. In non-perfect graphene, if mechanical strain is present, the resulting deformation of the crystal lattice can be described as a pseudo-magnetic field. Charge carriers propagating in such strained areas acquire an additional phase, similarly to the Aharonov-Bohm effect. The “twist” in the wavefunction due to this extra phase can lift the ban on complete backscattering, as we show in an optical experiment.

For the first time, we have presented experimental evidence that pseudospin effects have a dramatic influence on the double resonant Raman spectra, more precisely on the intensity of the D’ peak (see Fig. 1). Until now, this defect induced peak has only been observed for lattice defects (vacancy, grain boundary, etc.) and not for smooth potentials (pseudomagnetic field patterns). Each type of defect has a specific D’ peak to D peak intensity ratio, characteristic of the defect in question. We measure this fingerprint on crumpled single layer graphene and find an anomalously high D’ peak intensity. Since the D’ peak involves complete backscattering (see Fig. 1a), increased intensity is a hallmark of increased backscattering due to the pseudomagnetic field. Numerical calculations reproduce the measured “Raman fingerprint”, taking into account the pseudomagnetic field pattern produced by the crumpling (see Fig. 2).

Our results lead to a better understanding of charge carrier scattering in strained graphene. This is especially important, since strain fluctuations are thought to be the bottleneck limiting the mobility of high-quality graphene devices.
Figure 2: Calculated Raman spectra on crumpled graphene. (a) Molecular dynamics simulation of a twice folded rectangular graphene layer. (b) Calculated pseudo-magnetic field ($B_{ps}$) within the rectangular graphene layer. (c) Calculated peak intensities of the doubly resonant processes ($D$, $D'$, $2D$). For scattering on strain patterns (red peak), the calculation reproduces the measured $D'$ and $D$ peak intensities.

Related publication

DYNAMIC STRAIN IN GOLD NANOPARTICLE SUPPORTED GRAPHENE INDUCED BY FOCUSED LASER IRRADIATION

(OTKA-K119532)

A. Pálinkás, P. Kun, A. A. Koós, and Z. Osváth

Graphene on noble-metal nanostructures constitutes an attractive nanocomposite with possible applications in sensors or energy conversion. In this work we study the properties of hybrid graphene/gold nanoparticle structures by Raman spectroscopy and Scanning Probe Methods. While we found that successive high intensity laser irradiation increased gradually the doping and the defect concentration in SiO$_2$ supported graphene, the same irradiation procedure did not induce such irreversible effects in the graphene supported by gold nanoparticles (NPs). Moreover, the laser irradiation induced dynamic hydrostatic strain in the graphene on Au NPs, which turned out to be completely reversible. A thin gold film of 5 nm was deposited onto a SiO$_2$(285 nm)/Si substrate by an electron-beam evaporation system (AJA). Gold nanoparticles were formed on areas of 5×5 µm$^2$ by local laser heating of the gold layer using a confocal Raman microscope (WITec) and a focused, 6 mW laser-power @633 nm. CVD graphene was transferred onto the substrate (gold layer and gold NPs) using thermal release tape (TRT) method. Multiple Raman-spectroscopy measurements were performed on each selected region with low (0.6 mW) and high (6 mW) laser power. The samples' morphology was investigated by Atomic Force Microscopy both before and after the laser annealing.

The AFM image in Fig. 1a shows both the as-evaporated gold layer (left side) and an irradiated part (right side) with the borderline in the middle. Dome-like gold NPs formed on the irradiated part with diameter of 32 nm and height of 11 nm in average. Fig. 1b and 1c show AFM images of the same corner-like graphene edge, right after the transfer process and after multiple high power laser annealing, respectively. The initially formed nanoparticles remained unchanged after subsequent laser annealing (see for example the NPs marked with black crosses in Fig. 1. b-c, and the configuration of the NPs surrounding them). We can observe in Fig. 1b that the covering graphene is rippled in various longish shapes. In turn, in Fig. 1c the individual NPs are well outlined beneath the graphene, meaning that graphene follows better the shape of NPs after laser annealing. We performed successive Raman maps with 488 nm and 633 nm laser excitation on graphene/Au NPs in a 5×5 µm$^2$ area with 20×20 pixels. Low (0.6 mW) and high (6 mW) power measurements were performed alternately. The higher laser power was used explicitly to anneal locally the samples, while with low powers we characterized the effect of the applied heating.

Figure 1: (a) AFM image showing the border of as-evaporated (left) and annealed (right) gold region. (b-c) AFM images showing both graphene covered and bare gold NPs, b) before, and c) after subsequent laser annealing. The corner-like graphene edge is marked with red dashed line, white three individual bare gold NPs are marked with black symbols.

Figure 2: Correlation plot of the 2D-G Raman peak positions of (a) Au NPs supported and (b) Si/SiO$_2$ supported graphene. Subsequent Raman data measured with laser power of 0.6 mW (1, 3, 5) and 6 mW (2, 4).
In Fig. 2 we plotted the correlation plots of the 2D-G Raman peak positions of graphene. The average of the first low power measurement was at \((\omega_G; \omega_{2D}) = (1582.2; 2631.9 \text{ cm}^{-1})\), which corresponds to a small tensile strain \(\varepsilon_{\text{hidr1}} = 0.08\%\) and p-doping of \(E_F = -89\) meV. The following high power measurements (data sets no. 2 and 4) show a significant shift of both G and 2D peaks, which is nearly parallel with respect to the pure hydrostatic strain slope. We fitted the average values and found a slope of 2.37±0.02, which is close to 2.2 (the “strain” slope). Note that the effect is reproducible, the peak shifts are very similar in the two cases. The induced dynamic hydrostatic strain is \(\varepsilon_{\text{hidr2}} = 0.48\%\). Furthermore, the low power measurements are also very reproducible, the data sets no. 3 and 5 have averages close to the first one. On average, neither the strain nor the doping was changed significantly, as shown in Fig. 2a. For comparison, we prepared a sample where graphene was transferred directly to a standard, \(\text{SiO}_2(285 \text{ nm})/\text{Si}\) substrate. In Fig. 2b we plotted the corresponding 2D-G peak positions. After high intensity laser irradiation, significant increase in the p-type doping occurred, as is clearly seen from subsequent low intensity correlation plot data (sets no. 3 and 5, respectively). The shift of the averages follows the pure p-doping slope of 0.55 very well.

These results point out the role of the substrate in the laser irradiation induced effects on graphene, and can have implications in the development of graphene/plasmonic nanoparticle based high temperature sensors.

**Related publication**

OPTICAL VAPOUR SENSING ON SINGLE WING SCALES AND ON WHOLE WINGS OF THE ALBULINA METALLICA BUTTERFLY

(OTKA K 111741, OTKA K 115724)

K. Kertész, G. Piszter, Zs. Bálint, and L. P. Biró

Nowadays, monitoring the air quality of homes, work places, and industrial facilities is becoming more and more important. For the efficient characterization of the ambient atmosphere, gas and vapour sensors are required which combine high sensitivity and chemically selective detection of volatile organic compounds with low power consumption and fast response time and operate in ambient air. Sensors based on photonic-crystal–type nanoarchitectures may offer an optimal solution to this problem due to the fast development of the response signal (colour change) and relatively easy optical readout combined with small size.

The *Albulina metallica* butterfly species is specific in that males have structural colours on both of their wing surfaces (Fig. 1). In our earlier work, we showed that the vivid wing colorations are generated by quasi-ordered, “pepper-pot”–type photonic nanoarchitectures. We showed, that despite the almost-identical scanning electron microscope images of the photonic nanoarchitectures (Fig. 1), there are minor but characteristic differences between the two sides in respect to the size and distribution of the air holes filling the chitin matrix. Direct space analysis of the electron microscope images showed that the typical first-neighbour distance of the embedded air holes is characteristically different for the blue and gold-green wing scales causing the different structural colors.

![Figure 1: Photos of an imagine and scanning electron micrographs of wing scales of Albulina metallica male specimen. The (A) blue and (B) gold-green wing surfaces are shown.](image)

Selective chemical sensing of two qualitatively similar, but quantitatively different, “pepper-pot”–type photonic nanoarchitectures, which occur in the dorsal (blue) and ventral (gold-green) cover scales in the wings of the male *Albulina metallica* butterflies, were investigated using ten different vapours. The capillary condensation of vapours yielded characteristic response curves in relative reflectance both for the chemical substances and for the two different structures in the concentration range of 5% to 50% vapour in artificial air. This shows that, by combining different nanoarchitectures in an array of sensors, selectivity can be enhanced by using the “fingerprinting” of various vapours and storing the characteristic responses on the different elements of the array.

As the complete wings are optically complex objects, we also investigated the behaviour of single scales, both by using a microscope and collecting the signals not from the entire wing, but from one single scale only, and by removing single scales from the wing and placing them on microscope slides for individual characterization. Complete immersion of separated single scales in ethanol showed significant changes from blue to green, and from gold-green to red (Fig. 2A). We also performed vapour sensing measurements on ten blue and ten gold-green single wing scales while applying a 50% concentration of chloroform and water vapours. The average of the ten measurements on each side and for each vapour is plotted in Fig. 2B. It was shown, that single scales exhibit similar, chemically selective sensing both in reflected light and transmitted light as was found on the whole wings.

The effect of stacked wing scales on the vapour-sensing properties was also investigated. We measured transmittance of light across one, two, and three stacked scales during 50% ethanol vapour exposition. It was found that the optical response increases with the number of stacked scales showing that by increasing the volume of interaction between the vapours and the nanoarchitectures the sensitivity can be significantly enhanced.
Figure 2: (A) Reflected light optical micrographs of Albulina metallica single scales in air (upper) and submerged in ethanol (lower): the color changes from blue to green and from gold-green to red, respectively. (B) Average of vapour sensing signals (in reflected light) on single blue and gold-green Albulina metallica wing scales using 50% chloroform and water vapours, as noted. Measurements were performed on single scales still attached to the wing membrane.

These findings show that naturally tuned photonic nanoarchitectures can be used to construct miniature sensor arrays consisting of one or a few scale stacks with different chemical selectivity, enabling the production of small (approximately 100 µm size) and material specific vapour sensors with optical readout.
OPTICAL SPECTROSCOPY OF INDIVIDUAL NANOSCALE OBJECTS

(Hungarian Scientific Research Fund: FK-128327, KH-129578, K-112114 and K-119532)


The preparation and investigation of well-defined nanostructured materials contributes to a better understanding of their structure-property relationship. This is an essential background for the development of advanced functional systems in the field of photonics and optoelectronics.

In our research, we use a broad range of experimental approaches and techniques to prepare well-defined nanostructured materials and to study their interaction with light. In the highlighted projects we employ noble metal derived nanostructures, which show a very intense absorption and scattering due to the appearance of localized surface plasmon resonances. By combining optical microscopy, imaging spectroscopy and high sensitivity detection, we are able to carry out absorption or scattering measurements even down to the single nanoparticle level. This in turn allows access to a more rigorous interpretation of the relationship between the optical properties and the structure or surface properties of the investigated nanostructures.

One possible method for the preparation of nanostructured plasmonic surfaces is nanosphere templating of thermoplastic polymer layers. The gold-coated polymer replica of a Langmuir-Blodgett film consisting of sub-micron silica spheres can be used to create localized and propagating surface plasmons at the nanostructured substrate. This structure was used to investigate the signal enhancement related to indentations in the gold surface layer during micro-Raman scattering experiments. The indentations were prepared based on the above mentioned colloidal templating and the voids filled with 4-mercaptobenzoic acid (MBA) loaded gold nanospheres. The periodic void structure has been designed to allow selective excitation of a single void in a way that at the laser wavelength of the micro-Raman setup, the cavity-type plasmon modes localized at the metallic void interface can be effectively excited. The surface modification of the gold particles by MBA was studied in detail and the number of MBA molecules present on a single gold nanoparticle inferred from optical and electrophoretic-mobility measurements to be ca. 210. Correlative scanning electron microscopy and micro-Raman measurements allowed the investigations at the single void level. Raman signal from a single MBA loaded gold nanoparticle in the cavity was already detectable. The number of particles present at a single void-site provided a straightforward way to control the number of molecules excited during the experiments. By measuring the signal strength as a function of particle number, trapped inside a single nanovoid and comparing it with a reference sample (clusters of given number of particles on a flat gold surface), a 25-fold experimental signal enhancement attributed to the nanostructured nature of the interface could be inferred.

Figure 1: AFM image of the metallic void array (a) and a typical height profile across an individual void (b). Raman spectra obtained from exciting individual voids containing different number of MBA coated gold nanoparticles (c). Intensity of the 1578 cm\(^{-1}\) peak of MBA as a function of excited particle number measured on the nanostructured and the reference flat gold surface (d).
We are investigating the surface-chemical patch formation on individual gold nanorods. When thiol-group containing molecules are added to the sol of gold nanorods, they will bind irreversibly to the particle surface and replace any physically bound stabilizing ligands (cetyltrimethylammonium ammonium bromide in the present case). It is known from the literature that at sufficiently low concentration levels, these thiol-group containing molecules preferentially bind at the tip of the nanorods. In a recent study we have shown that correlative (measuring the very same objects) scanning-probe and optical micro-spectroscopic measurements performed on individual gold particles provide direct experimental evidence on the inhomogeneous ligand distribution of tip-selectively cysteamine-modified gold nanorods. At higher (10⁻² mM) cysteamine concentration, a well-defined patch is formed at the tips of the gold nanorods. At lower cysteamine concentration binding of the cysteamine still takes place at the rod tips, but it only provides a partial coverage, allowing other thiol molecules to bind at the rod tip. The findings allow for a more rational design of functional patchiness at the nanoparticle level.

Not only the spatially different molecular coating at the nanoparticle surface, but also local, nanometric substrate inhomogeneities might significantly influence the scattering spectra of supported plasmonic nanoparticles by means different plasmon resonance damping mechanisms. To study this in detail, ITO (Indium tin oxide) substrates were modified by the combination of nanosphere lithography and ion-bombardment to create a nanopattern with sharp boundaries between the irradiated and masked regions. Then, single particle scattering spectra of gold nanorods distributed over the nanopattern are investigated in detail. For nanorods located purely on either the masked or implanted areas, the spectra can be adequately interpreted in terms of a classical damped harmonic oscillator model, taking the chemical interface damping into account. When the particles overlap the masked and irradiated areas, however, markedly different behavior is found depending on the actual arrangement. For the rods experiencing a symmetric inhomogeneity (that is by bridging between two masked regions), damping varies smoothly with the extent of substrate inhomogeneity. For the asymmetric case (rods overlapping the boundary between the implanted and masked zones) a sudden increase of the damping is found, which is rather independent on the specific extent of substrate inhomogeneity. Comparing the damping variations with the related intensity changes indicates that substrate inhomogeneity at such length scales results in a different behavior than predicted by the classical damped harmonic oscillator model applied for nanoparticles encapsulated or homogeneously surrounded by molecular coatings.

Related publications
NON-DESTRUCTIVE EVALUATION SYSTEM FOR THE INSPECTION OF OPERATION-INDUCED MATERIAL DEGRADATION IN NUCLEAR POWER PLANTS

(EU H2020 - Grant agreement № 755330.)

A. Gasparics and G. Vértesy

The long-term operation (LTO) of existing nuclear power plants (NPPs) has already been accepted in many countries as a strategic objective to ensure adequate supply of electricity over the coming decades. In order to estimate the remaining useful lifetime of NPP components, LTO requires reliable tools. The objective of EU H2020 project: “Non-destructive Evaluation System for the Inspection of Operation-Induced Material Degradation in Nuclear Power Plants” (NOMAD – https://nomad-horizon2020.eu/) is the development, demonstration and validation of a non-destructive evaluation tool for the local and volumetric characterization of the embrittlement in operational reactor pressure vessels (RPVs). In order to address these objectives, the following steps will be taken:

− Development and demonstration of a non-destructive evaluation (NDE) tool for the characterization of RPV embrittlement, especially accounting for material heterogeneities and exceeding the existing information from surveillance programs.

− Extension of the existing database of RPV material degradation by adding correlations of mechanical, microstructural and NDE parameters as well as including quantification of reliability and uncertainty.

− Application of the developed tool to cladded material resembling the actual RPV inspection scenario.

NOMAD takes into account the priorities of reactor operation, responding to stringent safety requirements from regulators, and seeks to foster convergence of nuclear safety approaches. The approach to be developed within NOMAD will deliver information complementary to and exceeding the information obtained by destructive tests of surveillance samples, which are currently assumed to represent the whole component and do not take into account possible local material variations. NOMAD aims to fulfil requirements for nuclear safety in the framework of assessment of lifetime operation. Thereby, it covers the specific challenge and scope of the call: Continually improving safety and reliability of Generation II and III reactors.

The NOMAD consortium gathers nine important institutions in the field of European nuclear energy and development of the non-destructive techniques, all stakeholders in the assessment of the lifetime operation of NPPs. The consortium has been formed by Fraunhofer Institute for Non-destructive Testing IZFP (Germany, coordinator), SCK•CEN Belgian Nuclear Research Centre (Belgium), VTT Technical Research Centre of Finland Ltd. (Finland), SVTI Swiss Association for Technical Inspections (Switzerland), Coventry University (Great Britain), Hungarian Academy of Science - Centre for Energy Research (Hungary), Paul Scherrer Institut (Switzerland), Tecnatom S.A. (Spain), HEPENIX Technical Service Ltd. (Hungary).

Our institute contributes to the NOMAD project with own micromagnetic testing method: so called Magnetic Adaptive Testing (MAT). MAT is a recently developed method for non-destructive characterization of ferromagnetic materials which is based on systematic measurement and evaluation of minor magnetic hysteresis loops. This method will be tested and evaluated regarding its applicability for the determination of the material changes and the variation of the material properties during exposure to neutron irradiation.

As shown in our several previous research activities, MAT provides more sensitivity for material degradation than the major hysteresis loop and has an improved feature of measurement error suppression. An additional significant advantage of this method is that there is no need for magnetic saturation of the measured samples, which eases the practical application.

A specially designed Permeameter with a magnetizing/sensing yoke is applied for measurement of families of minor loops of the magnetic circuit differential permeability. The magnetizing coil is fed with a triangular waveform current with stepwise increasing amplitudes and with a fixed slope magnitude in all the triangles. The voltage signal in the pick-up coil is proportional to the differential permeability of the magnetic circuit. The MAT evaluation delivers large set of so-called magnetic descriptors from the measured data. The optimal descriptor as an output is selected by careful correlation analysis.

Even in the early phase of the project realization, we could obtain promising experimental results on Charpy and on block type specimens that were aged by thermal treatments or neutron irradiations. An example obtained on Charpy specimens are made of 22NiMoCr37 material can be seen in Figure 1; where the optimally selected MAT descriptor is seen as the function of the neutron fluence. Here we got monotonous correlation with the degree of irradiation, the scattering was ~5%, while the difference between samples irradiated by 5.1 x 10^{19} n/cm² and 1 x 10^{20} n/cm² achieved the 13% and 30%, respectively.
Figure 1: The output of the MAT method (the value of the descriptor) as the function of the independent parameter (neutron fluence) to be determined, in case of 22NiMoCr37 Charpy specimens

Related publications


Measurement of low contact angles is challenging. The investigated surface is immersed in the test liquid in case of the captive bubble method, therefore the characterization of swelling or porous layers is problematic. In case of the Wilhelmy balance method, the samples must have regular geometry and identical surfaces along the contact line, therefore coatings and thin films cannot be characterized. The developed indirect method combines the accuracy of the Wilhelmy method and the general usability of the sessile drop method.

The method is based on the use of a liquid bridge as a probe: the capillary bridge of the test liquid is stretched between the rim of the base of a cylinder and the investigated surface under equilibrium conditions. The advancing contact angle on the sample can be measured during the stepwise decrease of the bridge length. The receding contact angle is determined during the retraction of the cylinder. The contact angle is calculated from Delaunay’s analytical solution, while the necessary parameters are determined from the measured capillary force and from the automated analysis of the captured image of the liquid bridge. The contact angle on the cylinder’s rim changes continuously during the decrease and increase of the bridge length. The bridge is formed from a pendant drop. This unique feature ensures that the advancing contact line finds dry (not prewetted) surface.

Precalculated look-up tables were built up for nodoid type axisymmetric liquid bridges in the relevant parameter space. Parameter sensitivity investigations can be carried out based on these tables avoiding the difficulty of solution of the inverse problems. Another advantage of these tables can be found during the evaluation: the significant difference between measured and precalculated values indicates that the bridge is not axisymmetric or it is not in equilibrium. This verification ensures that the determined contact angle is reliable without the use of a second camera.

Figure 2: Sensitivity of the capillary force (F) and the contact radius (r) on the volume change of the capillary bridge. The colour bar shows the bridge volume. The capillary force of an evaporating liquid bridge can increase or decrease depending on the actual bridge geometry. The direction of change is determined by the change of the curvature of the nodoid surface.
The method was proved to be valid and highly sensitive, while its repeatability is so good as the repeatability of the sessile drop method with two times longer contact lines. The capability of the measurement of ultra-low contact angles was demonstrated on acid-treated superhydrophilic glass surfaces. The capillary force, as well as, the contact angle does not exhibit hysteresis on these surfaces. For more details, please refer:

N. Nagy: Contact angle determination on hydrophilic and superhydrophilic surfaces by using \( r-\theta \) type capillary bridges, *Langmuir*, under review.

![Figure 3: Capillary force and contact angle measured on an acid-treated glass slide. The capillary force does not exhibit hysteresis. The advancing and receding contact angles are equal within their standard deviation.](image)
IN SITU MONITORING OF ZrO₂ SURFACES DURING OXIDATION

(CAK, OTKA K115852)

P. Petrik, A. Romanenko, B. Kalas, L. Peter, T. Novotny, E. Perez-Fero, E. Agocs, T. Lohner, Z. Hozer, N. Nagy

One of the major applications of Zr is its use as cladding tubes in nuclear power plants. The corrosion and oxidation of different Zr alloys is an intensively investigated major safety issue. We used ellipsometry to characterize surfaces of zirconium tubes and plates for nuclear applications. We have shown earlier that ellipsometry can be used even on the surface of tubes with a diameter of 9.1 mm, when applying proper focusing. We also determined reference refractive indices for both zirconium and zirconium oxide, and demonstrated the capability of ellipsometry for the determination of the thickness and refractive index of the surface oxide applying different oxidation parameters. In this study, we characterized processed zirconium surfaces using the technique developed in our previous work. We used both ultra violet-visible-near infrared and mid-infrared ellipsometry to study the thicknesses of the surface layers as well as the dielectric functions of both the layers and the substrate. We also developed a heat cell that allows multiple angle of incidence ellipsometry measurement at elevated temperatures. We used this setup to monitor the temporal behaviour of hydrogenated and oxidized zirconium surfaces.

Figure 1: Left-hand side: Hydrogen-filled E125 zirconium wafer mounted on the heating stage in the cell for environmental ellipsometry. The ring-shaped spot in the middle of the wafer is the part that has been processed using electrochemical hydrogenation. Right-hand side: In situ ellipsometry measurements on three identical zirconium substrates of an E125 alloy processed under different conditions. The red curve shows the temperature profile. Blue curves are the A (phase shift – the ellipsometric angle that is more sensitive to the change of thickness of the surface layer) values measured by ellipsometry at the wavelength of 500 nm (dotted lines show measurement under Ar flow). The solid line is a measurement in air at a temperature of 28 °C and humidity of 41%. In the inset, showing the samples after the heat treatment, the different colours reveal different thicknesses of surface layers caused by oxidation.

Related publication

MULTILAYERS FOR TUNEABLE RESONANCE IN ELLIPSOMETRIC BIOSENSORS

(OTKA K115852 and M-ERA.NET WaterSafe)

B. Kalas, A. Romanenko, K. Ferencz, P. Petrik

For biosensing applications Bloch surface waves (BSW) can be utilized that are excited at the surface of one-dimensional photonic crystals (1DPC). In the ultraviolet (UV) wavelength range numerous proteins have characteristic absorption peak so measuring in this range selective measurements can be carried out. The main advantage of BSW-based sensors compared to the structures used in surface plasmon resonance (SPR) is the tuneability of the resonance wavelength at which the biosensor operates. The resonance wavelength can be easily tailored by changing the layer thicknesses or by modulating the optical properties of the applied materials. Other advantage of BSW is that by using 1DPC structures narrower dip and bigger propagation length (and thus enhanced biosensor performance) can be achieved in the wavelength spectra due to the small absorption (no metal layers are applied in the structures).

In this work we realised a structure by alternating SiO$_2$ and ZrO$_2$ nanolayers and thus we constructed a 1DPC suitable for biosensing application in the UV range. The optical measurements were carried out in a self-made Kretschmann-Raether flow cell combined with a spectroscopic ellipsometer (Woollam M-2000DI).

![Figure 1: The schematic figures of the 1DPC structures and the used flow cell](image1)

![Figure 2: The measured reflection map (normalized intensity of p-polarized reflection) of the 1DPC structure in the flow cell. The vertical axis shows the angle of incidence in degrees.](image2)

Related publication

SUSTAINABLE AUTONOMOUS SYSTEM FOR NITRITES/NITRATES AND HEAVY METALS MONITORING OF NATURAL WATER SOURCES

(„WaterSafe”, M-ERA.NET-2014, NKFI-OTKA: NN 117847)

M. Fried, A. Saftics, S. Kurunczi, P. Petrik, Z. Labadi

The international (with Romanian and University of Pannonia partners) project („WaterSafe”) aimed to develop a new autonomous system based on micro electrochemical sensors and ultra-thin solar cells for concentration measurement of different ionic species in natural water sources.

It focused on three directions: 1) new materials with high efficiency in solar energy harvesting and fabrication of small ultra-thin solar cells together with the power stabilizing device, able to supply the needed voltage to the sensors and electronics module; 2) new microsensors and materials for detection of nitrites/nitrates and heavy metals in water; 3) low cost autonomous energy system integration and fabrication.

We (MFA) investigated the developed (by University of Pannonia) metal-ion-bonding (Ni, As) special proteins (flagellar filaments) by optical (Spectroscopic Ellipsometry) and electrochemical (Cyclic Voltametry) methods. We performed promising electrochemical measurements with these new types of sensor-chips. The latest results were checked by comparative control measurements performed by partners from NANOM (Brasov, Romania), proving that the sensor-chip (protein) stability is good enough and even the sensor chips can be re-used after 1 month and chemical cleaning. This later investigation series prove that the prepared chips can be used after several months and more than once.

More information about the results of the project can be read on the webpage of the project: [http://www.icf.ro/pr_2016/WaterSafe/Obtained_results.html](http://www.icf.ro/pr_2016/WaterSafe/Obtained_results.html)
DIFFUSION AND REACTION KINETICS GOVERNING SURFACE BLISTERING IN RF SPUTTERED a-Si_xGe_1-x:H THIN FILMS

M. Serényi, A. Hámori and B. Kalas

The structural and surface quality of the material is one of the most critical issues regarding of their large scale application in electronic devices based on hydrogenated amorphous silicon (a-Si:H) [1], germanium (a-Ge:H) [2] and a-SiGe:H. Atomic hydrogen migration occurs in the amorphous network. The high temperatures applied during growth of those materials, e. g. during chemical vapour deposition, or device operations enhance the diffusion of H atoms, in particular of those liberated from their bonds to the host atoms. Such enhanced diffusion favours the migration of H atoms towards nanovoids where they very likely form molecular H_2 since the reaction 2MeH → H_2 + Me-Me is an exothermic one (Me indicates the host atom: Si or Ge). The accumulation on the wall of voids causes the evolution of hydrogen bubbles and then the formation of blisters. Some efforts have been made to understand the microscopic mechanisms determining the rupture of the MeH bonds and formation of H_2 rich voids at the origin of the blisters in order to prevent them. The objective of this work was to find a way to determine the threshold temperature below which surface blistering does not occur in hydrogenated a-Si_xGe_1-x, 0 ≤ x ≤ 1. This is achieved by a theoretical model that takes into account both the kinetics of the rupture of the MeH bonds and, in particular, the diffusion of the atomic H. The experimental results suggesting our theoretical approach have been obtained by Secondary Neutral Mass Spectrometry (SNMS) and by surface light reflectivity measurements, as regards of the time of the onset of blistering and its activation energy by Arrhenius plots. The data supplied by the latter plots allow the validation of the theoretical model. The calculated critical temperature for blistering is of the same order of magnitude as the experimentally observed one. The experimentally determined Vegard’s law-like dependence of the blistering activation energy [3,4] on the Si concentration in the a-Si_xGe_1-x alloys is interpreted by a simple formula and related 3D-like diagram.

Figure 1: SNMS depth profile of hydrogen in annealed a-Si and a-Ge layer after 40 minutes of annealing (a), and after 10 and 40 minutes in a-Si layer(b)

Figure 2: Graphical representation of blistering onset vs. temperature in a polar coordinate system. The left-hand vertical plane belongs to the Si and the right one to the Ge Arrhenius plot.

Related publications


Makyoh Topography

Ferenc Riesz

Makyoh topography is an optical tool for the qualitative flatness testing of specular surfaces, based on the defocused detection of a collimated light beam reflected from the tested surface. By inserting a square grid into the path of the illuminating beam, the height map can be calculated by integrating the gradients obtained from the distortion of the grid’s reflected image (quantitative extension).

In the past year, activities were concentrated both on methodology and applications.

Applying the grid creates not only the structured illumination necessary to calculate the large-scale surface shape, but aids in qualitative visual evaluation as well. If the grid’s image is sharp, the simultaneous qualitative observation of the sample morphology in high resolution is possible within the same image, in addition to the low-resolution height map. We have studied the conditions for this sharpness [rie18]. A sharpness criterion was given based on a wave optics model, while the necessary instrumental settings were calculated using geometrical optics. In addition, it was shown that only lens-based set-ups allow positioning of the grid to be sharp on the Makyoh image; for mirror-based set-ups this is not possible because of geometrical instrumental constraints (Fig. 1).

For in-house research, deformation measurements of Si-based thin-film (SiO_x, SiN_x) structures were performed for stress evaluation.

Related publication

Refractive Index Variation of Magnetron-Sputtered a-Si$_{1-x}$Ge$_x$ by “One-Sample Concept” Combinatory

(OTKA K115852 and M-ERA.NET WaterSafe)

T. Lohner, B. Kalas, P. Petrik, Z. Zolnai, M. Serényi and G. Sáfrán

Gradient a-Si$_{1-x}$Ge$_x$ layers have been deposited by “one-sample concept” combinatorial DC magnetron sputtering onto one-inch-long silicon slabs (Fig. 1). Characterizations by electron microscopy, ion beam analysis and ellipsometry show that the layers are amorphous with a uniform thickness, small roughness and compositions from $x = 0$ to $x = 1$ changing linearly with the lateral position.

By focused-beam mapping ellipsometry we show that the optical constants also vary linearly with the lateral position, implying that the optical constants are linear functions of the composition (Fig. 2). Both the refractive index and the extinction coefficient can be varied in a broad range for a large spectral region. The precise control and the knowledge of layer properties as a function of composition is of primary importance in many applications from solar cells to sensors.

Figure 1: Set-up used for the combinatorial deposition of the a-Si$_{1-x}$Ge$_x$ layer

Figure 2: Atomic fraction as a function of position along the center line of the combinatorial sample measured by Rutherford backscattering spectrometry. The black dotted line shows the distribution of the atomic fractions of Si and Ge based on the calibration using energy dispersive spectrometry (EDS) in a scanning electron microscopy.
KoFAH - ADVANCED FUNCTIONAL MATERIALS FOR AUTONOMOUS SENSOR NETWORKS


In 2018, we continued the work on i) piezoelectric thin films, ii) piezo-MEMS sensors and vibrational energy harvesters as well as on iii) the integration of sensor node demonstrators, such as vibration analyser, tyre sensor, and intelligent bondage. The project parallelly comprises all three levels: material (i), device (ii) and system (iii).

Material: piezoelectric thin films

In order to conduct research on advanced CMOS compatible piezoelectric thin films a new sputtering system was purchased and installed. Apart from general use of the tool the project-specific goal is to deposit piezoelectric AlN, and alloyed XAlN (X=Sc, Cr, etc.) layers. High quality piezoelectric layers are essential components of the micro-vibration energy harvesters and actuators targeted by the project.

The setup containing three-magnetrons with the appropriate SW enable both automatic and manual operation. Two of the magnetrons can be operated in DC or pulse DC mode, whereas the third one is working in RF mode. The system can handle various size substrates ranging from small pieces up to 6” wafers. The ultimate vacuum of the load-lock equipped deposition chamber is < 1x10^-7 mbar. Deposition or reactive deposition of single layers and multilayer structures as well as co-deposition is also possible.

The related tender was successfully completed in 2017 and the contract with VAKSIS Co, Turkey signed in September 2017. In order to provide the required footprint and services our staff removed an outdated system and reorganized the lab. The company delivered and installed the system in due time (May 2018), so the introduced technology became an organic part of the processing line (Fig. 1.). Though special emphasis was put on the formation of piezoelectric layers, other projects will also benefit from the facility.

The optimization of AlN deposition conditions through more than 50 tests led to a reasonable trade-off between deposition rate (400-500 nm/h) and thickness uniformity (±2-3%), whereas the optimum sample temperature was found to be around 300 °C. According to cross-sectional SEM analysis and X-ray diffraction the optimized AlN layers show columnar crystal structure with high degree of c-axis orientation. The obtained longitudinal piezoelectric charge constant was around 3 pC/N for 0.7-1.4 um thick AlN, which agrees well with literature data. These preliminary tests provide a solid starting point for the upcoming research on high-piezoelectric-constant XAlN alloys.

Device:

a) Piezo-MEMS sensors

In 2018 we continued the work on spiral shaped piezo-MEMS accelerometers and started research also on metal substrate based vibrational energy harvesters. In the former part we demonstrated a low-volume, stress-free, piezoelectric micro-electromechanical system (MEMS) cantilever array for fully implantable hearing aids [1]. The 9-element spiral-matrix is sensitive to middle part of audible frequency range (1200-2300Hz) through the proper resonant frequency of the individual spirals tuned by dimensions of the cantilevers based on the results of Comsol simulations.
Moreover, each spiral was designed with a multielectrode structure fitted to various mode shapes (Fig 3) to collect more than one ambient frequencies with a single cantilever.

Figure 2: 9-element wire bonded Fermat-spiral array (a) and two typical cantilevers (four- and three-turn types, b and c, respectively)

Figure 3: Simulation of various mode designs for multi-frequency accelerometers to optimize the electrode positions

The test device was fabricated by a 30-step micromachining process. Fermat spiral geometry ensures the reduced device footprint, which was formed by deep-reactive ion etching (DRIE). The uniformity of cantilever thickness is controlled by the Si-on-Insulator (SOI) wafer. The biocompatible piezoelectric material aluminum nitride (AlN) was deposited by reactive radio frequency (RF) sputtering from an AlN target.

The fundamental resonances and upper harmonics were collected for each cantilever by the laser Doppler vibrometer at the Technical University of Vienna. During the measurement the cantilevers were mounted on a minishaker which was excited by white-noise signal. The results show a good agreement between the theoretical and measured frequencies. In 2019, we will measure the generated electrical signal vs. the excitation frequency and acceleration, and test the mode selectivity of the optimized electrodes.

Figure 4: Laser Doppler vibrometer input voltage during white-noise excitation. The resonant frequencies fall in the range of 1200-2300 Hz (a) and harmonics in 3000-5200 Hz (b) depending on the geometry.
b) Piezo-on-metal harvester

As a second objective of the Device work-package, we started to optimize piezo-cantilevers for energy harvesting as well. In order to supply sufficient electrical power for autonomous sensor nodes using RF communication we need energy harvesters larger than the standard MEMS structures. For the 1-10 cm² area-range standard Si based technology is often found to be too expensive. Moreover, in harsh vibrational environment and for demanding applications, such as medical implants, the mechanical robustness of single crystalline Si is insufficient.

![Image of Ni and stainless-steel cantilever arrays after laser cutting](image1)

![Image of measurement setup](image2)

Figure 5: Ni and stainless-steel cantilever arrays after laser cutting (left upper and centre image) and the geometrically fitting stencil mask for top contact deposition (bottom left image) (a). Measurement setup for testing the output voltage and power of the piezo/metal harvester at controlled frequency and acceleration (b).

Hence, our aim was to combine MEMS technology with metal substrates. Stainless steel has a 50 times higher fracture toughness than single crystal Si. Moreover, the cantilever geometry was shaped at room temperature by high precision stencil laser cutting tool by our industrial partner (Alpha Assembly), which provides an economic technology compared to Si 3D micromachining. As harvester substrates we compared Ni (100 µm) and stainless-steel (SUS 304, 80 and 120 µm) sheets. Figure 5a shows the Ni and stainless-steel cantilever arrays. The length of the cantilevers was varied between 12-22 mm, expecting resonance frequencies in the 150-650 Hz range.

The simplified fabrication technology was implemented in the cleanroom. Pulsed DC sputtered AlN piezo layer of 1.2 µm was deposited first in our new vacuum system (Vakis) followed by the electron beam deposition of the top electrode through a stencil mask (Fig. 5a). Individual cantilever beams were simply cut by scissors and wire bonded before mounting them on the shaker based measurement setup (Fig. 5b). The obtained open circuit voltage was 430 mV at an acceleration of 9.81 m/s² (1G) for the 18 mm cantilever at resonance (201 Hz). At an optimal load resistance of 220 kΩ and output power of 540 µW was obtained [2], which requires significant improvement in 2019. Nevertheless, we could demonstrate a simple, room temperature hybrid fabrication process for metal-MEMS harvesters.

System:

a) Tyre deformation monitor

3D MEMS force sensors mounted at the internal sidewalls of vehicle tyres continuously provide information about the actual mechanical deformation of the tyre in operation (Fig. 6). The monitoring of the elastic deformation and its sudden changes offers feedback about the load and friction via characterizing the shape of the tyre sidewalls.

![Diagram of communication module and readout electronics](image3)

Figure 6: The integrated tyre monitoring test tool

The tyre deformation on a vehicle is proportional to the acting forces on the wheel – longitudinal, lateral, and vertical - carrying information on the contact between the tyre and road surface (figure 7). The accomplished application uses RF communication between the rotating wheels and vehicle control. The signal per rotation depends on the number of sensors mounted in the
wheel. The sampling frequency of 100 Hz fits well with the sampling frequency of the CAN bus communication of a car. We also integrated an RF coil for external charging of the battery of the readout electronics.

![Graph showing the correlation between the out-of-balance voltages of the 3D force sensor and the acting forces on the tyre.](image)

*Figure 7: The correlation between the out-of-balance voltages of the 3D force sensor and the acting forces on the tyre.*

A tyre equipped with an integrated sensor is being used on an autonomous Nissan Leaf for the preliminary test in co-operation with MTA SZTAKI (Fig. 8). Among the other positive results, we demonstrated the long operating lifetime of the system by operating the sensor for >100 km running mileage.

![Image of a tyre mounted on a Nissan Leaf with the readout electronics placed in the trunk during the charging process.](image)

*Figure 8: The test tyre mounted on the Nissan Leaf with the readout electronics placed in the trunk during the charging process.*

b) Vibration analyser

Our vibration analyser – or VibrAn for short – is a complex, wireless, ambient energy powered and easy-to-use solution for vibration analysis. It was designed to incorporate the latest commercial technologies and achievements in the field of energy harvesting and wireless sensor networks with an emphasis on energy efficient spectrum estimation algorithms for embedded systems. This solution is implemented on a small printed circuit board and contains all the necessary commercial circuit components for hybrid energy harvesting; acceleration sensing; data acquisition, data storage and analysis; as well as wireless communication (Fig. 9) [3].

The on-board microcontroller was programmed to select the most energy-efficient data handling algorithm (direct transfer or embedded analysis) based on the weighed combination of user settings and ambient energy (Fig. 10). We tested and calibrated the system in laboratory environment with reference sensors, as well as on a vibrating duct in order to simulate real life applications.
The accelerometer is able to measure vibrations up to 100 Hz without aliasing, however, around 200 Hz it is guaranteed to appear. The maximum extracted power from the piezoelectric beam was 781 µW with resistive load, and 244 µW with complex load (energy management IC). The highest measured efficiency of the energy management chip (BQ25570) was 81%. In order to perform a 2000 data acceleration measurement (with RF data transmission) with the system 30 mW average power was needed. If this measurement was to be solely powered by energy harvesting, it would around 2-3 hours would be required to harvest the necessary amount of energy. In the real life application (Fig. 11) we managed to harvest a total of 2.25 mJ energy in 4 hours and 20 minutes.

The presented small device consists of commercially available components, provides an interface to study and test vibrational energy harvesters. In order to maximize the harvested energy, the main vibrational frequency of the piezoelectric cantilever can be tuned by a moving mass. The proposed system can support the R&D on energy harvesters by providing an interface to test new designs. Future work will focus on improving energy harvesting by incorporating our own energy harvester and decreasing RF communication power consumption by designing our own low power RF protocol. The final target is to achieve an autonomous system transforming the ambient energy into electrical energy.

**Related publications**


INVESTIGATION OF MEMRISTIVE STRUCTURES


Resistive switches or memristors are two terminal passive electric components, whose resistance can be reversibly varied between two or several states by the voltage is applied. They are built as a capacitor like metal-insulator-metal structure, in which the two electrodes are connected by a conductive filament of nanometer dimension. Despite their simple structure they show complex operation, which offers many promising applications. Using them as simple memory cell (RRAM) is close to commercialization. Memristors have approached or even exceeded the specifications of contemporary flash memories. However, their more promising complex applications, such as their integration as memory and processing unit in neuromorphic computing are still subjects of intensive research.

The NEMS group joined the cooperation with the group of András Halbritter at the Department of Physics of BME in studying resistive switches in 2017. That group has large experience in characterization of memristive systems (Ag₂S, AgI, SiOₓ, or Nb₂O₅) using an STM arrangement. Relying on our nanofabrication expertise and facilities, the target of this collaboration is the development, characterization and optimization of on-chip resistive switches. The devices were initially fabricated by electron beam lithography, then further scaled down to <10 nm by controlled electrical breakdown process. Recently nanofabricated Ag₂S and SiOₓ resistive switches were successfully prepared and this research was continued in 2018. The devices are fabricated at MFA while the electrical characterizations are performed at BME. In 2018 OTKA grant (K 128534) was obtained for the collaborative research on nanometer scale resistive switching memory devices lead by András Halbritter.

In case of Ag based resistive switching devices the 1/f type noise was studied at BME using the STM setup vs. the surrounding solid electrolyte (Ag₂S, AgI). As control experiments noise measurements were performed on pure Ag nanowires lacking any resistive switching media (see Figure 1, black dots). These Ag nanobridges were lithographically designed at MFA and thinned by feedback-controlled electromigration technique (see insets of Figure 1). The measurements revealed that the magnitude of the noise not, only the total resistance does depend on the surrounding material. This result implies that the noise arises from the internal fluctuation of the Ag nanowire rather than from environmental effects. The resistance dependence of the noise is quantitatively captured by a theoretical model (fitted lines in Figure 1). The article is under review at Nanoscale.

Figure 1: The current noise ratio values as a function of the mean resistance. Ag nano filaments were formed in STM based Ag₂S (yellow) and AgI (purple) memristive nanojunctions, as well as in pure Ag MCBJs (grey) and electromigrated Ag nanobridges (black). The blue and red lines represent the best fit to the Ag₂S data.

In SiOₓ, memristors the switching is based on the amorphization and crystallization of a Si rich region. In this memristive system a dead time effect can be observed: once the device is switched OFF, it is blocked in the OFF state for the period of the dead time. Tuning its length would have essential role in the application of SiOₓ RRAM. Based on our paper, published in 2017, we further investigated the nature of the dead time. The measurements revealed that the dead time shows clear dependence on the pressure, but the Ar plasma treatment of the SiOₓ surface has no effect, whatsoever. Furthermore, an aging effect was observed, as we “wrote and erased the device” several times, the length of the dead time increased.

Similar to the Ag based memristors, noise measurements were performed on graphene-SiOₓ resistive switching devices. The active region of the SiOₓ switch is formed between graphene electrodes in a gap of few nm (see red region in Figure 2.c). This nanogap is created by electrical breakdown of initially contiguous graphene nanostripe, cut by electron-beam lithography.
(Figure 2a). By optimizing the geometry of the patterned graphene and the electrical breakdown protocol, we could break the graphene constrictions in a controlled way. The constrictions could be narrowed step by step and finally few nm (<5 nm) dimension gaps were generated. The low-frequency 1/f type noise was measured at several stages of the breakdown process and finally obtained in the tunnelling regime. Afterwards, the SiO$_x$ switching site was formed in the nanogap, and the noise was measured at the different memristor states. This systematic measurement allows the separation of the noise by the graphene electrodes from the noise of the resistive switch. In the near future noise measurement during the dead time is planned.

**Figure 2:** Illustration of the processing steps for forming of a nanometer-dimension SiO$_x$ switch

Besides both memristive systems above, transition metal-oxides such as niobium oxide, tantalum oxide, vanadium oxide are also well-established resistive switching compounds. We plan to study those memristive systems at ultrasmall dimensions. The size limits for well controlled RRAM operation have to be established. Since BME had a significant experience in Nb$_2$O$_5$ layer contacted in STM arrangement, it was the first material, which was realized in on-chip implementation. In the Nanotechnology laboratory several devices were fabricated to study the effects of the structure (vertical or lateral arrangement) and electrode materials (graphene, gold, niobium). The structures were patterned by electron beam lithography, while the niobium oxide was deposited by reactive sputtering. The test measurements showed promising results, we could reproduce the same switching effects as observed in the STM arrangement. In the near future further optimizations are needed to result in more stable devices. Fabrication and process optimisation of VO$_2$ based samples is also in progress.
In this work we show the role of large-angle dual scattering (DS) events appearing as a wide background in the medium energy ion scattering (MEIS) spectra of gold nanostructures. The facility at the International Institute of Accelerator Applications at Huddersfield, UK, has been used for the analysis of thin Au layers deposited on glass substrate and plasmonic Au-silica core-shell nanoparticles (NPs) deposited on Si substrate. The typical Au layer thickness was 10-20 nm and the core/shell nanoparticle size was 25/40 nm. MEIS analysis has been performed with 100 keV He\(^+\) ions for scattering angles of 90° and 125°. Note, these conditions are standard in MEIS experiments. In the size range of 10-100 nm, both for thin layers and spherical particles, besides small-angle multiple scattering, large-angle dual (and plural) scattering also gives strongly increasing contribution to the single scattering (SS) spectra of gold. The estimation of the DS yield is essential for quantitative spectrum evaluation and preliminary optimization of the measurement conditions.

The single scattering MEIS spectra of planar Au layers and spherical Au nanoparticles were simulated with the RBS-MAST [1] and SIMNRA [2] codes, considering the detailed 3D sample geometry. The surface roughness of the Au layers and the spherical shape and first neighbour configuration of the nanoparticles was considered. Atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM) have been applied as complementary characterization methods.

In our case dual scattering offers significant yield in a wide energy range, which consists of (i) an additional peak overlapping the single scattering spectra of gold and (ii) a smooth low energy background overlapping the glass or Si substrate signal. For 90° and 125° scattering angles the DS peak to SS peak ratios in the (i) energy range seem to be quite similar. The low energy (ii) DS yields, however, strongly differ resulting in 10-15%, and only 2-3% signal levels compared to the corresponding SS peak heights for the two different scattering angles.

We estimate the DS yield contribution in two different manners: with individual particle trajectory simulations provided by the SIMNRA code [2], and with calculations based on a simplified geometrical model for DS events using parametrized functions for He\(^+\) stopping, cross-sections, and charge neutralization processes [3]. For planar Au layers SIMNRA simulations and the results of the simplified geometrical model show good agreement for the dual scattering yields. Similar DS yield calculations had been performed for thin ZnO and Cu\(_2\)O layers [4]. The results show that the procedure can be applied for a wide range of different materials in the calculation of MEIS spectra.

**Figure 1:** MEIS spectra of a 10 nm Au/2 nm Cr\(_2\)O\(_3\)/glass layer system and SIMNRA simulations with only single scattering (SS) and single+dual scattering (SS+DS) calculations. The green line shows the low energy part of the spectrum according to our simple geometrical model for dual scattering [3]. Neutralization for the incoming He\(^+\) projectiles is considered in the calculations.
Figure 2: Same as it is in Fig. 1 but for a 20 nm Au/2 nm Cr₂O₃/glass substrate system.

Figure 3: MEIS spectra of a monolayer of 25 nm diameter Au core/9 nm thick silica shell spherical nanoparticles deposited on Si substrate and 3D spectrum simulations with only single scattering (SS) and single+dual scattering (SS+DS) calculations. SS yields are calculated with RBS-MAST while DS yields are with SIMNRA, respectively. The green lines show the low energy part of the spectra according to our simple geometrical model for dual scattering [3].

Related publications

ECSEL JU “POSITION-II project, “Towards Next Generation of Smart Catheters and Implants”

(A pilot line for the next generation of smart catheters and implants — POSITION-II, H2020-ECSEL-2017-1-RIA-two-stage-783132)

P. Fürjes, O. Bálint-Hakkel, I. Bársony, F. Bíró, P. Földesy, Z. Hajnal, P. Hermann, V. Rakovics, I. Réti, Z. Szabó

The POSITION-II project is to realize a breakthrough in Europe in the development of smart catheters with embedded functions. By the introduction of open Flex to Rigid (F2R) technology platforms for miniaturization, in-tip AD conversion, wireless communication, MEMS transducer technology and encapsulation novel systems for minimal invasive surgery and medical examination will be developed. The availability of these open platforms will allow manufacturers to improve the performance of smart catheters at a lower cost and will enable the development of completely new minimally invasive smart instruments. The 46 member European consortium is led by Philips.

Our group was invited upon the previous successful cooperation in the ECSEL “INCITE” project where together with the Polish Foundation of Cardiac Surgery Development (FRK) and the Polymer Engineering group of BME we jointly developed a laparoscope demo system with tweezers integrated force sensor chips and electronics.

In the present project our group has two tasks:

− Design and development of a 3D Flex-to-Rigid compatible force sensor for tip head integration of the catheter, where, alternative solutions will be evaluated and realized in response to the need of capacitive transduction. Similarly to the piezoresistive force sensor we developed in the frame the INCITE project. A force-transfer and -amplifier rod will be formed from the handle layer of the SOI wafer, whereas the deforming membrane will be the 40µm thick device layer with isolated read-out capacitors on top. In this early phase of the project model calculations and preliminary experiments are being led to finalize the design, elaborate specific processing steps as well as the F2R compatible process flow.

− Material selection and process development for encapsulation and evaluation for biocompatible protective coatings of complex electronic devices to be implanted in the human body. Our contribution is the design and production of test chips and involvement in performing in-vivo tests.

Our general goal is to elaborate a capacitive type force sensor on flexible substrates. This will open the way towards various future applications in medical and robotic fields forming the basis of joint developments with domestic industrial partners in medium term.
LOW POWER COMBUSTIBLE-TYPE NANOSENSORS FOR GAS DETECTION IN HARSH ENVIRONMENT

(Hungarian-Russian Collaborative Research Program is 2017-2.3.4-TéT-RU-2017-00006)

P. Fürjes, O. Bálint-Hakkel, I. Bárcsony, F. Bíró, P. Földesy, Z. Hajnal, P. Hermann, V. Rakovics, I. Réti, Z. Szabó

On the basis of our previous results summarized in the excellent PhD work of Ferenc Bíró about processing of micro-hotplates and micro calorimetric gas sensors, a bilateral collaboration with the group of National Research Nuclear University MEPHI (Moscow Engineering Physics Institute) was initiated. Our joint R&D proposal was positively evaluated in both countries and the three year project started officially on April 1st, 2018 with the final goal to develop the prototype of solid state micro gas sensors for detection of hydrocarbons, CO and NH₃ concentrations up to their lower explosion limits.

In the first year the micro-hotplate structure was further improved to minimize its power consumption and temperature non-uniformities by means of novel filament geometries and applying new materials. The detrimental effect of temperature gradients arising along the filament and across the hotplate was proven. The operation temperature reduction to 500°C or below plays crucial role in mass transport related degradation effects. Catalysts operating efficiently at reduced temperature is also essential part of the work. This task is shared with the Russian partner and subject of the 2nd year of the project. In the reporting period

1. The geometry of the Pt filament for uniform temperature was modified and temperature gradients < 0.5°C/µm towards the perimeter were reduced. Thereby the masstransport was minimized and the lifetime of the sensor is expected to exceed the minimum one year. The heat sink contact wire was introduced in the centre the conventional double-spiral geometry modified such as to provide extra power along the perimeter of the heated area. Both versions have small variations in filament diameter and widths to find the best structure. Some of the characteristic designs are shown in Fig 1. A new patterning technology of the Pt filament was also introduced replacing the lift-off technique by a dry etching process of Pt in our DRIE system using Ar-SF₆ gas mixture. The perfect patterns and sidewalls facilitate further processing, eliminate sidewall flakes, increase yield and uniformity of filament. Identical filament pairs are badly needed in the Wheatstone-bridge configuration of the final device.

Figure 1: Mask images of selected filament geometries for formation of uniform temperature hotplates

2. Uniform and reproducible crystalline Si filaments were formed from SOI (silicon on insulator) wafers using the buried oxide for achieving uniform thickness and identical geometry. Cantilevers are suspended on stress compensated SiO₂-Si₃N₄ membrane to eliminate possible ruptures of the cantilevers. Compared to metals higher resistivity of device silicon ensures higher filament resistance at the same temperature i.e. the cross section of the current routes should be increased to achieve the sufficient resistance. With the c-Si based design the electromigration can be reduced by > two orders of magnitude.

The heated area of these filaments can be completely covered on both sides with catalyst or passive pastes by drop deposition
Figure 2: Suspended silicon filaments layouts and the layer stack below.

Observing the resistance variations and also the “all-around” catalyst deposition, two filament geometries were designed (Fig. 2 top). The layer structure is identical for both filament geometries. The top side of the filaments are covered with Si₃N₄-SiO₂ layers, while the bottom side is covered with the buried oxide (Fig. 2 bottom). The silicon-nitride is the diffusion barrier against oxidation of silicon at the top, consequently in this design we expect the oxidation of the silicon filament to occur only at the bottom side reducing the resistance drift. The processing of the first test wafer will be expected end of January 2019.

Related publications

BIOMECHANICAL TISSUE CHARACTERIZATION BY FORCE SENSITIVE SMART LAPAROSCOPE OF ROBIN HEART SURGICAL ROBOT

(Intelligent Catheters in Advanced Systems for Interventions - INCITE, ENIAC CALL 2013-1 (partners: Philips Research – The Netherlands, FRK – Poland, BME))

P. Fürjes, O. Bálint-Hakkel, I. Bársony, F. Bíró, P. Földesy, Z. Hajnal, P. Hermann, V. Rakovics, I. Réti, Z. Szabó

To obtain real-time multi-parametric information about physical and anatomic conditions of affected tissues during Minimal Invasive Surgery (MIS) operation is crucial for precision and safety. [1] The integrated 3D force and tactile sensors should provide these information about the different organs and tissues touched.

Integrated 3D force sensors for Minimal Invasive Surgery applications

Piezoresistive vectorial force sensors were designed according to the proposed force ranges and manufactured by 3D bulk micromachining process [2]. Two different MEMS sensors were electro-mechanically integrated into a metal laparoscope tweezers with the pre-processing electronics for analogue-digital data conversion and communication with the robot control system (Fig. 1-1). The sensors were embedded in biocompatible elastic polymer.

Biomechanical measurements by robot integrated laparoscope

Tissue hardness measurements were performed using real animal tissue perpendicularly touched with the gripper. The signals of the tip tactile sensor were collected and analysed with reference to a constant uniform protrusion of the laparoscope (Fig. 1-2).
The measured force values clearly indicate the contact depth and the mechanical characteristics of the tissue. When pressing the soft muscle a continuous increase of force was detected starting with a slight slope. When the hard bone was pressed, a higher slope is recorded directly from the starting point on. The tissue-characteristic force signals offer the possibility of their automatic distinction.

A simple setup was constructed to mimic blood vessel and check whether the sensor built in the grasper is able to identify an artery by measuring the pulses. A liquid filled silicone tube was grasped and the signals of the force sensor were recorded along with pressure sensor readings while the microfluidic pump was operating in pulsed mode. Fig. 1-3 demonstrates that the sensitivity of the measurement depends on the preset clamping force, as expected from the blood pressure measurement protocol.

![Image of grasping force sensors and pressure sensor signals](image)

**Figure 3:** The signals of the grasping force sensors and the pressure sensor built in the fluidic system when applying pulse mode pressure. The three series are taken using different preset grasping forces.

### Summary

Studies of the prototype “smart” sensory laparoscopes have verified their usefulness in real-time force feedback robotic systems by identifying the state of tissue and determining the clamping force of the grasper in a surgical system. Implementing this “smart” tool into the surgery robot system, the human-machine synergy was also demonstrated by the Polish partner by applying two-directional haptic control.

### References


### Related publications


POLYMER MICROFLUIDIC SYSTEMS FOR MEDICAL DIAGNOSTICS

(KTIA VKSZ_14-1-2015-0004)

P. Fürjes, O. Bálint-Hakkel, I. Bársony, F. Bíró, P. Földesy, Z. Hajnal, P. Hermann, V. Rakovics, I. Réti, Z. Szabó

Precise and fast PoC monitoring of disease related blood marker molecule or bacteria levels could be crucial in effective therapies. In a dedicated Lab-on-a-Chip (LoC) solution the microfluidic system has to transport the sample and the washing buffer to the active area of the chip, while mixing and incubating the sample with the reagents. As incubation and read-out require specified timing, precise sample handling and flow control are essential. The use of biological sample also requires bio-inert surface properties with minimized non-specific adsorption and coagulation in the channels. We target to develop a polymer based microfluidic cartridge for autonomously controlled sample transport in an integrated bioanalytical device. [1]

Autonomous microfluidic systems for blood protein detection

A microfluidic system was designed and manufactured for transporting whole blood or plasma at a precisely controlled sample rate to be integrated into Point-of-Care Lab-on-a-Chip based diagnostic devices. The detection of cardiovascular diseases was in focus in cooperation with 77 Elektronika Ltd. In the “Multiparaméteres Point of Care in vitro diagnosztikai rendszerek fejlesztése” project a specific microfluidic system was designed, actually the geometry was modified to fulfill requirements of optical detection with real blood sample. Accordingly, a new, microfluidic system compatible with the bioanalytical specifications (sample volume, targeted detection limits, surface blocking, etc.) had to be designed. With the 77 Elektronika Kft. we are developing Lab-on-a-Chip based diagnostic device for a specific project of the Science University of Pécs to support human in-vitro fertilisation also.

Figure 1: Microfluidic cartridge for testing of autonomous sample transport and preparation

The material composition of the laboratory stage / pre-industrial cartridge was optimised for the required sample flow rate, the optical and mechanical properties. The embedding protocol of PDMS-PEO molecules was modified considering the molecular weight, concentration and physical parameters of the PDMS polymerisation process (temperature, time, surface treatments of the molding master).

Surface modification of polymers compatible with industrial fabrication technologies

Our laboratory has been involved in the development of precision injection molding technology and surface modification processes of micro structured polymer cartridges. Hydrophilic and non-fouling features are crucial requirements of the autonomous fluid sample transport in the microfluidic cassette, therefore surface modification of the polymer substrate is necessary. We conducted wet and dry chemistry experiments to create adequate surfaces. The surfaces were characterised using several surface analytical methods. The long term stability of the surfaces was examined by contact angle measurements. Surface chemistry functional groups were identified by Attenuated Total Reflectance Fourier Transformed Infrared (ATR FT-IR) spectroscopy. The morphology was inferred from Atomic Force Microscopy (AFM) images, whereas the thickness and homogeneity monitored by ellipsometry. The modified surfaces retained their hydrophilic character for two months period. (Figure 2).
The ATR FT-IR spectra showed that a homogenous hydrophobic layer could be formed on the polymer surface by wet chemical methods. Evaluation of the ellipsometry and AFM measurements revealed that the thickness of the layer is typically ~100-200 nm (depending on the parameters of the preparation).

**High resolution silicon mold insert for injection molding microfluidic systems**

Our research laboratory is participating in development precise micro-injection molding of plastics for high throughput fabrication of microfluidic systems in cooperation with the 77 Elektronika Kft. and Z-Microsystems GmbH. The applicability of the technology is not trivial for fabrication microstructures, as the definition of the molding parameters and the development of molding master is quite critical. The MEMS Lab developed a reliable technology for fabrication molding master using bulk silicon micromachining technology by 3D Deep Reactive Ion Etching (DRIE) of crystalline silicon wafer. The final structure was developed by DRIE with adequate surface roughness and wall angle for the injection molding technique. The geometry transfer achieved by the developed molding master is demonstrated in Figure 3.

**Related publications**


Finite Element Modelling and Simulation in the Development of MEMS and Microfluidics Devices

P. Fürjes, O. Bálint-Hakkel, I. Bársony, F. Bíró, P. Földesy, Z. Hajnal, P. Hermann, V. Rakovics, I. Réti, Z. Szabó

Initial design as well as specific optimization tasks mostly involve not only the careful structural and process engineering, but also various simulations of device operation in microtechnology. Numerical simulations enable assessment of stability of the device components under various external conditions, as well as trial modifications of the studied devices, adaptation to varying requirements, etc.

Modelling and simulation also has the advantage of lower resource needs and faster trial evaluation cycles. In the following we present a couple of examples of applied models and simulations, carried out in the COMSOL finite element modelling (FEM) framework. FEM provides approximations of arbitrary accuracy for device and environmental components. Systems of coupled partial differential equations can be numerically solved in practically any configuration of device components and environmental conditions, with simplifying assumptions about the local behaviour of the various state-functions and physical variables. As multiple physical quantities are being simultaneously solved for in the iterations of the simulations, hence their colloquial name, multiphysics.

Figure 1: Time steps (from left to right: 0.02, 0.08, 0.14, 0.20 ms) of water entering a surface modified capillary channel. The channel width is 200 µm, height is 50 µm. The bottom of the farther part of the channel is modified by cylindrical steps of 2 µm height. In the beginning only the closer half of the channel is filled by the liquid, during the time steps the changes in form and gradual progress of the air/water interface are well observable. Comparison of various surface morphologies is ongoing.

Effect of the surface morphology on capillary flow in microfluidic channels

Control of fluid flow in microchannels has been a field of intense development in the past decade. A promising direction is the changing of wetting properties by modification of surface morphology in the channel to accelerate (or decelerate) the progress of the fluid surface at desired regions. Numerical adjustment of the interface geometry to the fluid properties and desired control parameters requires several time-dependent simulations of the behaviour of the fluid (most of the times air-water) system.
Optical Mach-Zender Interferometer (MZI) form the basic unit of the detecting layer of a glass supported Lab-on a Chip cassette. Based on prior optical simulations we formed waveguide structures with 2×2 μm² cross-section on a glass support (Figure 1). We used epoxy based resists (SU-8, DWL and EpoCore) which were selected by the consortium members. Devices suitable for optical characterization were formed by using available photolithography technology.

Besides optimizing the parameters of the individual steps of the lithography process (time and dose of the exposure, mask distance, baking temperature), we also conducted experiments with different cladding layers (SU-8, EpoClad). We verified the morphology and the adhesion of the wave guide layers by Scanning Electron Microscopy (SEM). Following the successful implementation of this part of the project the MZI containing cassettes were given to the consortium partners for functional tests.

In the next stage of the development we will investigate the possibility of embedding the microstructures in material systems which are compatible with industrial technologies.
CELL AND PARTICLE MANIPULATION AND SCREENING IN MICROFLUIDIC SYSTEMS

(OTKA CK 83821, VEKOP-2.2.1-16-2017-00001)

P. Fürjes, O. Bálint-Hakkel, I. Bársony, F. Bíró, P. Földesy, Z. Hajnal, P. Hermann, V. Rakovics, I. Réti, Z. Szabó

The demand for microfluidics enabling fast and effective preparation and analysis of liquid samples in microscale diagnostic (Lab-on-a-Chip) systems underlined the importance of studying these phenomena. Due to the governing physical phenomena on microscale, classical sample preparation methods, such as efficient mixing of fluids as well as size-dependent separation and sorting or filtering of corpuscles in the liquid samples becomes a challenge. Novel microfluidic structures have to be developed based on the physical laws of this size domain.

Development microfluidic system for efficient separation circulating tumour cells (CTC)

In cooperation with the research groups of István Rajta and András Guttmann we participated in the design and fabrication of special microfluidic systems dedicated to sorting and separation circulating tumour cells. The channel system containing 3D tilted pillar structures of high specific surface was designed according to the results of preliminary Finite Element Modelling. The behaviour of the fabricated microfluidic system was defined by analysis of the movement of human tumour cells, to validate the FEM simulation. The computational fluid dynamics (CFD) assisted chip design and the entire microfabrication process was demonstrated with some preliminary test results on flow characteristics.

As a continuation of our previously published work, we presented a detailed evaluation of a microfabricated cell capture device utilizing a doubly tilted micropillar array. The device was fabricated using a novel hybrid technology based on the combination of proton beam writing and conventional lithography techniques. The resulting unique hybrid device had a small central region with the doubly tilted micropillar array for improved cell capture, fabricated by PBW (proton beam writing), while the surrounding area of the chip was generated using UV lithography. This novel combination extended the potential of conventional microstructuring techniques, generating high interest both from engineering and biological application points of views. Tilted pillars offer unique flow characteristics and support enhanced fluidic interaction for improved immunoaffinity based cell capture. The performance of the microdevice was evaluated by an image sequence analysis based in-house developed single-cell tracking system. Individual cell tracking allowed in-depth analysis of the cell–chip surface interaction mechanism from hydrodynamic point of view. Simulation results were validated by using the hybrid device and the optimized surface functionalization procedure. Finally, the cell capture capability of this new generation microdevice was demonstrated by efficiently arresting cells from a HT29 cell-line suspension.

Modelling and characterisation of droplet generation, trapping and detection in impedance based cell analytical microfluidic system

Droplet based microfluidics have developing relevance in the field of Lab-on-a-Chip technology. In these multi-phase flow devices, the continuous sheath emulsion enables to generate, manipulate, mix, focus and separate encapsulated chemical reagents or biosamples as assay of living cells. Therefore, cell-analytical and diagnostic procedures can be automatized on microscale, although the precise control and monitoring of droplet parameters and behaviour are essential for their reliable...
application. Accordingly, this work focuses on design and characterisation of a hybrid polymer microfluidic system having integrated electrode system (Fig. 2). The developed system is capable of creating, manipulating, trapping and monitoring droplets having precisely determined size fitted to general cell diameter. [2, 3]

The influence of flow characteristics of two-phase microfluidic systems was analysed regarding the droplet generation, particle encapsulation and trapping processes. Droplets were dispersed in oil continuous phase with the requirement of precise size distribution to enable effective cell entrapment controlled by the applied flow parameters. Hydrodynamic behaviour of the microfluidic system was modelled by Finite Element Method (FEM) using COMSOL Multiphysics and compared to experimental results. The applicability of droplet based cell encapsulation and hydrodynamic trapping and the capability of impedance spectroscopy based droplet and cell detection were also characterised.

References


Related publications

SOLID STATE NANOPORE AND NANOCAPILLAR BASED BIOANALYTICAL SYSTEMS

(KTIA VKSZ_14-1-2015-0004)

P. Fürjes, O. Bálint-Hakkel, I. Bársony, F. Bíró, P. Földesy, Z. Hajnal, P. Hermann, V. Rakovics, I. Réti, Z. Szabó

Nanoporous membranes are fundamental components of the transport modulation based label free electrochemical biosensors envisioned for high sensitive molecule detection. [1] The sensitivity and the specificity of these sensors are significantly affected by the pore geometry what has to be fitted to the size and conformation of the target molecules. Precise tailoring of nanopore geometries and alignment to target molecule conformation and size improves the signal-to-noise level of the identification method - in our case the electrochemical impedance spectroscopy (EIS). The pore geometry engineering is essential for reliable and reproducible manufacturing of integrable solid state nanopore-arrays in molecule diagnostic devices. Other important issue is the adequate selection of the applied material composition. Commercialization of the nanopore based biosensors or Lab-on-a-Chip devices seems to depend on the development of precise and high throughput nanofabrication techniques enabling reliable and reproducible shaping of nanopore geometries in extremely thin, but mechanically stable solid state membranes having electrical resistance as high as possible:

- Different (5-10nm thick TiO$_2$, AlO$_x$ and HfO$_2$) dielectric layers were deposited by ALD (atomic layer deposition) and tested electronically to select the adequate insulation layer to be able to integrate multi-electrode array for EIS measurements.

![Figure 1: Integrated electrodes for on-chip EIS measurement](image)

**Related publication**

SURFACE-ENHANCED RAMAN SCATTERING ACTIVE PERIODIC 3D STRUCTURE FOR TRAPPING AND HIGH SENSITIVE MOLECULAR ANALYSIS OF PARTICLES OR CELLS

P. Fürjes, O. Bálint-Hakkel, I. Bársony, F. Bíró, P. Főldesy, Z. Hajnal, P. Hermann, V. Rakovics, I. Réti, Z. Szabó

Raman spectroscopy is finding many applications in biology, life sciences and other areas. Raman scattering is inherently weak, but its sensitivity can be improved by implementing surface-enhanced Raman scattering (SERS). SERS evolves in the vicinity of nanostructured metallic surfaces or nanostructures achieving several orders of magnitude enhancement in the Raman signal and extremely improved sensitivity reaching the attomolar (10⁻¹⁸ M) concentration ranges [1]. This highly sensitive detection performance of SERS was utilized for analysing molecules located in the few nanometer distance or immobilised on the surface of micro and nanoparticles trapped in a specially designed microstructure.

In a previous work the highly sensitive molecule recognition performance of a specially designed SERS substrate was demonstrated. The general inverse pyramid structures were fabricated as cavities in perforated membrane applicable for particle and cell filtering, sorting and trapping. In the voids of the gold covered substrate size compatible particles functionalised by different molecules were trapped, their SERS signal was detected and the different molecules were recognised.

The fluorescent molecules were analysed by SERS utilizing the plasmonic enhancement by the structured surface of the traps. The definite and sensitive differentiation of the molecules immobilized on the polystyrene bead surfaces are presented in Figure 2, where a huge increase in the Raman signal can be observed on the SERS surface.

Figure 1: Fluorescent beads with appropriate 2µm diameter (Sigma Aldrich - green and Spherotech - blue) entrapped in the periodic array of perforated pyramidal structures: multichannel fluorescent (left) and SEM image (right)

Figure 2: Comparison of the SERS spectra recorded on the clean SERS substrate (black) and different fluorescent beads on silicon (red) and trapped in the periodic array (blue). SA – Sigma Aldrich and ST - Spherotech fluorescent beads, respectively
In our approach special size fitted SERS active substrate was prepared by micromachining techniques in silicon wafer to be applicable for particle entrapment. Subsequently, gold nanospheres were trapped in the pyramidal cavities. SERS performance of the hierarchically combined structures was analysed and compared by using a highly diluted benzophenone solution and octadecanethiol surface functionalization. The recorder spectra are demonstrated in Fig. 3.

Figure 3: Scanning electron microscopic images of the periodic array of gold coated inverse pyramids with the entrapped gold nanoparticle (left). Reference normal Raman (right, curve a) and surface enhanced Raman spectra of benzophenone recorded on array of gold coated inverse pyramids (right, curve b). array of gold coated inverse pyramids with entrapped nanoparticles (right curve c) and the latter with octadecanethiol surface functionalization (right, curve d).

The applicability of special periodic 3D structure was demonstrated for simultaneous particle (or cell) or nanoparticles trapping and extremely sensitive Surface-Enhanced Raman Spectroscopy based detection of molecules immobilized on the surfaces of the confined beads.

References


Related publications


[2] I. Rigó, M. Veres, P. Fürjes: SERS active periodic 3D structure for trapping and high sensitive Raman-spectroscopy of molecular surface analysis of particles or cells, Lab-on-a-Chip Europe 2018 Conference, Rotterdam, The Netherlands, 2018
INTELLIGENT WOUND PATCH FOR ONLINE MONITORING WOUND HEALING PROCESSES – WOUNDER

(National Research, Development and Innovation Fund (NKFIA) via NVKP_16-1-2016-0018)

P. Fürjes, O. Bálint-Hakkel, I. Bársy, F. Bíró, P. Földesy, Z. Hajnal, P. Hermann, V. Rakovics, I. Réti, Z. Szabó

In the clinical practice, the proper care of wounds obtained in accidents, postoperative and ulcerative ulcers is of primary importance. It is a basic expectation of the treating physician to obtain continuous or regular information on the healing of the wound. In case of a home-based hospitalization, the control of wound is time consuming and difficult for the physician, but remote monitoring of the appropriate parameters can help in effective curing. The task of the “intelligent bond” we developed is to facilitate the work of the physician and the cure of the patient by monitoring the process of healing. In case of a problem the user and the physician should be warned about the need for a check or a replacement.

An intelligent tool was developed to provide continuous information about various parameters of the wound healing, such as temperature, humidity, and the tightness of the bandage. [1] Targeting a final wireless, point-of-care application we focused on the minimisation of the energy consumption of the electronics. Appropriate sensors were chosen and integrated into a flexible PCB. Low power consumption electronics were also developed to solve the preliminary signal processing and communication tasks using Bluetooth protocol. Data processing and visualisation software was also developed. For testing the proper functionality of the sensor system, as well as their influence on the operation behaviour of the sensors various tests and calibrations were elaborated by using different wound dressings applied in medical practice.

![Figure 1](image-url)

Figure 1: Flexible PCB for sensors (a) and signal processing electronics (b) for wound healing monitoring system. The sensor data can be visualized in the application specific software (c) – WoundER / PC.

Related publication

INVESTIGATION OF METAL (Ni) INDUCED LATERAL CRYSTALLIZATION OF AMORPHOUS Si THIN FILMS AT LOW TEMPERATURE

(TÉT-10-1-2011-0570)

G. Z. Radnóczí, B. Pécz, I. Stoimenos, N. Frangis, N. Vouroutzis (AU, Thessaloniki)

The well-known Metal Induced Lateral Crystallization (MILC) process was studied at low temperature to characterize the various ways of crystallization taking part in the process. At low temperature crystallization is dominated by the movement of the NiSi$_2$ particles forming the characteristic whiskers (Figure 1a). Further growth of the whisker sidewalls is suppressed in contrast to experiments carried out at higher temperatures. Consequently, the morphology of the resulting crystalline structure will be dominated by whiskers growing in various directions. Whiskers growing in 111-type directions often change growth direction to other equivalent 111-type direction forming a 70.5°kink.

Tetrahedral NiSi$_2$ inclusions forming during crystallization and previously observed in Si whiskers grown by the MILC process were also observed in these experiments confirming that the whisker growth is very similar to other experiments (Figure 1b).

Analytical measurements were also carried out using the newly installed Themis microscope’s SuperX detector system to confirm the presence of Ni at whisker tips. Unfortunately, the preparation process (etching the glass substrate under the 50 nm thick a-Si/Si film) mostly removed the NiSi$_2$ clusters leading the whisker growth, however in some exceptional cases enough silicide was preserved. Such a whisker tip is imaged in STEM-HAADF mode and shown in the figure below together with the elemental map for Ni and Si (Figure 1c).

![Figure 1](image_url)

**Figure 1:** a.) HAADF overview image of a group of mostly parallel whiskers. Black regions at the whisker tips are holes where the NiSi$_2$ clusters were etched during preparation. b.) an exceptional whisker with a preserved NiSi$_2$ cluster showing as a bright region due to Z-contrast and c.) EDX elemental map of Ni and Si of the region imaged in b.)

Related publication

DESIGN OF CORROSION RESISTIVE SiC NANO-LAYERS

A. S. Rácz, M. Menyhárd

We have demonstrated earlier that applying ion beam induced mixing (IBM) at room temperature on C/Si/C/Si/C multilayer structures nano-sized SiC production occurred. It has also been shown that the appearance of nano-sized SiC rich layer improves considerably the corrosion resistance of the irradiated sample. A correlation between the corrosion resistance of the sample and the amount and distribution of SiC determined by AES depth profiling has been found [A.S. Racz et al., ACS Appl. Mater. Interfaces, 2017, 51, 44892–44899]. This observation provides the possibility of tailoring corrosion resistance of a given sample; one must determine and produce the SiC amount and distribution necessary to reach the desired corrosion resistance. If one wishes to design a protective coating allowing for various constrains concerning the layer structure, determining the optimal irradiation conditions using an experimental approach is rather time consuming and expensive, however. Therefore, we looked for applying simulation techniques.

Here we report on corrosion resistance measurements on samples produced by IBM at room temperature applying various irradiation conditions and samples containing C and Si layers of various thicknesses and numbers being on Si substrate. For ion bombardment we have used the easily available Ar⁺ and Xe⁺ ions. The amount and distribution of the SiC has been determined by TRIDYN simulation (not by AES depth profiling). The effective areal density of SiC (introduced in our previous work) was calculated from the SiC distribution and an excellent correlation between these quantities and the measured corrosion resistances has been found (Figure 1). Therefore, having any request for a given corrosion resistance by the help of the TRIDYN simulation we can determine the irradiation conditions considering the other constrains by the layer thicknesses and numbers as well. This enables a high freedom for the design of the protective coating layer.

![Figure 1: The experimentally measured corrosion rate vs. effective areal density of SiC determined by TRIDYN simulation; inset enlarged y axis.](image)

Related publication

HIGHLY SAFE GaN METAL-OXIDE-SEMICONDUCTOR TRANSISTOR SWITCH

(SAFEMOST)

L. Tóth, Zs. Fogarassy, I. Cora, D. Gregušová (IEE), J. Kuzmík (IEE) and B. Pécz

In the frame of the international SAFEMOST project we continued the complex structural study of the InGaN/AlGaN/GaN heterostructures prepared by our colleagues at IEE SAS, Bratislava. The main goal was to influence the electrical polarization of the layers through incorporation of a suitable mechanical stress and thus reaching normally-off operation of the switching device.

In 2018, installation of a new aberration corrected TEM (of the type FEI Themis) in our lab opened new possibilities in our characterization spectrum. The use of the aberration corrected objective lens improved the point-to-point resolution by a factor of two (down to 0.09 nm). Also, use of several new methodologies (like scanning transmission techniques with various detectors, EDS mapping, etc.) became possible in the lab.

By applying the new Themis electron microscope, local variation of the of the strain tensor components were determined using geometrical phase analysis (GPA) technique (Figure 1). Starting from high resolution images of the cross-sectional specimens and their Fourier transform, the in-plane and out-of-plane deformation components of the crystal lattice were calculated with a special software (relative to a non-deformed reference area in the same TEM lamella). It turned out that the in-plane strain component is practically zero, while the out-of-plane component followed the chemical composition of the layer structure. This means large negative strain in the AlN layer, small (1-2%) negative change in the AlGaN, and somewhat larger (3-4%) positive strain in the InGaN film (Figure 2). The elemental maps taken with the EDS system confirmed our observation. This result supports the model of the Slovakian colleagues on the polarization effects observed by electrical measurements. These samples were found be suitable for the realization of normally-off MOS HEMT (High-electron-mobility transistors) after some additional processing steps. 
Figure 2: High resolution micrograph of the InGaN/AlGaN/GaN cross sectional sample taken with the new 200 kV Themis electron microscope used for the above GPA analysis.
IN SITU TEM AND EX SITU HEATING EXPERIMENTS ON K-GA₂O₃

(MTA Postdoctoral Fellowship and bilateral CNR-MTA)

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Ga₂O₃ is a wide bandgap semiconducting oxide (~4.7 eV), promising for UV optoelectronics and power electronics. Ga₂O₃ layers were grown onto (001) surface of α-Al₂O₃ by vapour phase epitaxy [1]. Ex situ heated samples up to 1000 °C and studied by XRD, DSC, TEM and simulations using JEMS software package. The in situ heating of cross sectional and plan view TEM lamella was also done in TEM up to 980°C in order to follow and study the κ→β (orthorhombic to monoclinic) structural transformation.

The structure of κ-Ga₂O₃ is ordered in 5-10 nm large (110)-twinned domains, and each domain has an orthorhombic structure with Pna₂₁ space group symmetry [2]. This phase is a new polymorph among the Ga-oxides.

During the in situ heating experiment the structural changes and the transformation was acquired on movie and the samples were studied in detail (BF, HRTEM, SAED, simulations). Fornari et al. [3] earlier studied the DSC curve of the transformation and they reported a weak endothermic bent up to 650 °C. We connect this bent to the moving of grain/twin boundaries, antiphase boundaries, and the enlargement of domain size in the material. Between the very spectacular κ→β phase transformation we identified no amorphous phase.

The kinetically driven phase transformation from κ to β is topotaxial, since the direction of the oxygen stacking is the same. We determined the structural relationship between the two phase and we modelled the interface. Beside the β and κ, the metastable γ phase also appears at lateral interface between β/κ and next to κ as well.

With the ex situ heating (up to 820°C with 2°C/min speed) of κ-Ga₂O₃ we had another transformation. We found the κ→γ phase transformation (Figure 1). The γ-Ga₂O₃ is cubic metastable phase. We studied its crystal structure by HRTEM and SAED and concluded a most probable crystal structure of it. The interface between them was also studied.

Figure 1: The interface of the transformation on HRTEM image in the middle. Left from the interface ('A') the symmetry averaged, filtered HRTEM image of γ phase with the simulated one for comparison. Right from the interface ('B') is the same but for the κ-Ga₂O₃.

Related publications
THE INFLUENCE OF BATH ADDITIVES ON THE THERMAL STABILITY OF NANOCRYSTALLINE Ni FILMS PROCESSED BY ELECTRODEPOSITION

T. Kolonits (MFA, ELTE, PhD student), L. Péter (Wigner), I. Bakonyi (Wigner), J. Gubicza (ELTE, supervisor) and Zs. Czigány (MFA, supervisor)

The effect of various organic additives (such as saccharin and trisodium-cytrate) on the microstructure (grain size, dislocation and twin densities), mechanical properties and thermal stability of electrodeposited Ni films was investigated by X-ray diffraction (XRD) line profile analysis and transmission electron microscopy (TEM). The main task of the project is to investigate the thermal stability of different initial microstructures which could be formed by solving organic additives in the original electrolyte.

The electrodeposited layers were deposited at room temperature at low current density onto copper substrate. The basic electrolyte mainly contained nickel-sulphate (NiSO$_4$·7 H$_2$O) and boric acid (H$_3$BO$_3$). XRD and TEM grain size and phase analysis was carried out to determine the microstructure. Hardness tests were made to examine the mechanical properties. Heat treatment (at 400, 500, 600, 750 and 1000 K) was applied to investigate the stability of the micro and macro properties.

According to our former research [1] even a small amount of organic additives has a significant effect on the microstructure (grain size, defect density and texture) of nanocrystalline Ni films. In this work three different microstructures were formed: the organic additive free bath resulted a large grain size (90-130 nm), a low dislocation density (13 × 10$^{14}$ m$^{-2}$) and a (220) type texture. Trisodium citrate resulted a moderate grain size (60-80 nm) and dislocation density (30 × 10$^{14}$ m$^{-2}$) and the direction of the texture was changed into (200). The additive saccharin resulted in the smallest grain size (20-30 nm), the largest defect density (160 × 10$^{14}$ m$^{-2}$), the highest hardness and the texture was eliminated. The differences were caused by the presence of incorporating sulphur and sodium [1].

The changes of the hardness and the microstructure can be followed on Figure 1. It was found that the layer with additive saccharin which showed the highest hardness on room temperature has the worst thermal stability since the high defect density led to a large driving force for recrystallization; the recrystallization process occurred between 750-1000 K and took place in a few minutes. The best thermal stability was achieved in the layer processed with trisodium-cytrate as recrystallization has not been observed even after heating up to 1000 K.

![Figure 1: Hardness, dislocation density and crystallite size of heat treated electrodeposited nanocrystalline nickel layers](image)

Related publication

STRUCTURE AND MECHANICAL PROPERTIES OF HARD AND TOUGH WBC LAYERS – POSSIBLE INDUSTRIAL APPLICATION

S. Mirzaei (Brno), M. Alishahi (Brno), P. Soucek (Brno), L. Zábransky (Brno), V. Buršíková (Brno), M. Stupavská (Brno), V. Peřina (Rež), K. Balázsi (MFA), Zs. Czigány (MFA), P. Vašina (Brno)

A cooperation of Thin Film Physics Dpt. and Dpt. of Physical Electronics Masaryk University is running since 2016 in research of tungsten boron carbide (WBC) thin films. The main challenge in deposition of protective coatings to produce films, which simultaneously exhibit high hardness and enhanced fracture toughness. Nowadays, popular ceramic based protective coatings show difficulties to cope with these increased demands due to their inherent brittleness. Materials exhibiting such seemingly contradictory combination of mechanical properties - high hardness and moderate ductility - was already realized experimentally in Mo$_2$BC and recently predicted by ab-initio calculations in crystalline X$_2$BC system (X = Ti, V, Zr, Nb, Mo, Hf, Ta, W). Our aim is to produce fracture tough WBC protective coatings and in the long run to produce the theoretically predicted W$_2$BC crystalline phase which was predicted to have the best mechanical properties in the X$_2$BC family. However, low enthalpy of formation of W$_2$BC phase and existence of WB and WC phases instead of W$_2$BC phase indicate difficulties of deposition of crystalline W$_2$BC phase. Our results were published in Surface and Coatings Technology [1,2]. In these two papers we have investigated the mechanical, bonding and structural properties of the film at fixed C content with variation of B/W ratio and constant B content with changing C/W ratio, especially in the vicinity of the composition range of W$_2$BC.

WBC films were deposited by combination of DC magnetron sputtering of W and B$_4$C targets and pulsed DC sputtering for C in Ar at 500ºC. The pulsed regime resulted in 2.5 times increase of ion flux at 350 kHz and 65% duty cycle compared with DC sputtering. Bonding structure and mechanical properties were investigated by XPS and nanoindentation, respectively. Structural properties were investigated by TEM (including HRTEM and SAED) using JEOL3010 equipment at MFA. It was determined, that the coatings far from the composition of W$_2$BC phase are amorphous, while those coatings close to W$_2$BC composition are nanocomposites containing nanocrystals with size of ~5nm embedded into an amorphous matrix (Figure 1). A certain level of short range ordering can be observed even in the amorphous films which is manifested in short, curved and irregular lattice fringes in the HRTEM images. All the layers exhibited high hardness (>20GPa) so they all can be classified as hard coatings. The level of crystallinity played no crucial role in determining the hardness of the coating, while the effect of the coating structure and bonding was clear - the densest coating with the highest relative amount of W-B bonds exhibited the highest hardness of ~ 29 GPa (Figure 2).

We are planning to continue the research with coatings deposited in industrial deposition chamber and other members of X$_2$BC family (e.g. Mo$_2$BC).

Figure 1: HRTEM image and SAED pattern of W$_{22}$B$_{17}$C$_{30}$ film. The film has nanocomposite structure with nanocrystals embedded in the amorphous matrix.

Figure 2: Hardness and Young's modulus correlates with fraction of stiff W-B bonds for sputter deposited W$_x$B$_{70-x}$C$_{30}$ coatings

Related publications


New Type Functional Alloy Films

(NT OA-112156)

F. Misják, K. Hajagos-Nagy, M. Čaplovičová (Slovak University of Technology in Bratislava)
G. Radnóczi

Effect of growth temperature on the growth of CoCrFeNiCu high entropy alloy (HEA) films

Five-component CoCrFeNiCu HEA films were deposited by DC magnetron sputtering using spark-melted targets at background pressure of $6 \times 10^{-8}$ mbar with a deposition rate of $\sim 10$ nm/min. The working pressure was $3 \times 10^{-3}$ mbar by applying 99.9 % pure Argon as sputtering gas. Films were deposited onto thermally oxidized (100)-oriented Si wafers. The growth was carried out at room temperature, as well as, elevated temperature of 380 °C.

The nanostructure of the films was analyzed by transmission electron microscopy (TEM) in a Philips CM20 microscope at 200 kV accelerating voltage. HREM measurements were made in a 200 kV JEOL JEM ARM 200cF microscope. Samples for TEM investigation were produced in cross section views, embedding the films in Ti rings and grinded by mechanical polishing to about 50 μm thickness. The thinning was then followed by Ar+ ion milling at grazing incidence.

The structure of the films grown at room temperature is single-phase FCC and corresponds to zone T structure, with a well expressed $<111>$ texture. Width of the columns is uniform about $\sim 25$ nm and the growth competition region is about 50 nm thick in the 500 nm thick film. The columns are rather defective, the main defects are planar defects, stacking faults and twin lamellae. Their density is very high; it is around 2-3 faults/nm (Figure 1). As the film is grown in good vacuum conditions ($p=6 \times 10^{-8}$ mbar) no impurity effects are expected to be present. The impingement rate of oxygen/metallic species is $\sim 5 \times 10^{-3}$. The five-constituent components are randomly distributed in the FCC structure; no ordering or separation of components is detected.

The morphology of the film grown at 380 °C substrate temperature corresponds to the transition between zones II and III of the structure zone model and possesses dominant single phase FCC structure. Repeated nucleation is clearly observed (Figure 2a), meaning the formation of a covering or blocking layer during the growth of alloy crystallites.

![Figure 1: Overall (a) and high resolution (b) image of CrFeCoNiCu alloy film grown at 20°C substrate temperature and 6x10^{-8} mbar background pressure](image)
This is also supported by the random crystallographic orientation of the grains. The vacuum during growth was maintained at \(p=4\times10^{-6}\) mbar, resulting in an impingement ratio of impurity to metal species \(~1\times10^{-1}\).

This impingement ratio can result in the formation of a covering layer (either oxide or nitride or their mixture) leading to repeated nucleation. The FFT (Fast Fourier Transform) obtained from the high resolution image shows the presence of the FCC reflections (those falling on the rings in Figure 2b) but shows the presence of other reflections as well, indicating the formation of second crystalline phases in the film. Their quantity is however small, as they are not detectable in the overall diffraction patterns obtained from the film.
TEM STUDY OF COPPER SILICIDES

E. Dódony (PhD student), G. Z. Radnóczi (supervisor)

Copper-silicides attracted considerable interest due to their wide range of applications. Cu$_3$Si is an important phase of the family (Figure 11). It is used in ultrapure silicon synthesis for photovoltaic and electric devices, as contact material in microelectronics and as catalyst for carbon nanowire and semiconductor production. Despite the importance of copper-silicides, their phase and structural relations are not entirely solved yet. Due to their importance, we are studying the formation of copper-silicides in thin amorphous silicon (a-Si) films. A 10 nm thick a-Si film was transferred to copper grid (Cu-grid) and heated in-situ in a Philips CM20 transmission electron microscope. During the heating the Cu-grid acted as an unlimited source for the diffusion of metal into the a-Si film. Silicide formation started at 500 °C (Figure 2). We observed the η-Cu$_3$Si-phase and its modulations during our experiments.

![Figure 1: Structural model of Cu$_3$Si; space group: P-3m1, a$_c$: 4.06 Å, c$_c$: 7.33 Å](image)

![Figure 2: Raw [100] projected experimental HRTEM image of modulated Cu$_3$Si with four times of the (100) periodicity (= 14.0 Å) of the basic structure (a), its Fourier-transform (b) and the Fourier-filtered experimental image (c)](image)

For the phase and structural measurements, we recorded high resolution (HRTEM) images and selected area electron diffraction (SAED) patterns, under Jeol3010 and Philips CM20 transmission electron microscopes, respectively. By analysing SAED patterns and HR images, we found that the η-phase’s structural model does not fit our experimental data and that many modulations of the phase formed under the experimental conditions.

Through measurements, calculations and modelling we gave a new structural model for the η-Cu$_3$Si-phase (Figure 1) and solved two of the many modulations formed by the different ordering of the Cu – Si atoms forming supercells. One is shown in Figure 2 with modulation in the a direction with four times periodicity of the basic Cu$_3$Si structure.
THE INFLUENCE OF ARTIFICIAL AGING ON THE MICROSTRUCTURE OF AN AL-ZN-MG-ZR ALLOY PROCESSED BY EQUAL CHANNEL ANGULAR PRESSING

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There is a large interest in age-hardenable Al-Zn-Mg alloys (7xxx series) due to their technological and practical importance, as these alloys can be treated to have a preferable combination of ductility and strength, as well as reasonable weldability and corrosion resistance. If a supersaturated Al-Zn-Mg alloy is aged under different conditions, various metastable and stable precipitates may form. Therefore, aging can be used for tailoring mechanical behaviour of these alloys. Although, the microstructure obtained by equal channel angular pressing (ECAP) has been extensively studied in the literature, the effect of artificial aging on the precipitation and the strength of SPD-processed supersaturated Al-Zn-Mg alloys has not been clarified so far.

In this paper, the effect of artificial aging on the microstructure and hardness of an ultrafine-grained (UFG) Al-4.8%Zn-1.2%Mg-0.14%Zr (wt. %) alloy was studied. The UFG microstructure with an average grain size of about 260 nm was obtained by severe plastic deformation (SPD) applying four passes of ECAP at room temperature. Then, artificial aging was performed on the ECAP-processed samples at 120 °C and 170 °C for 2 h.

The size and morphology of the matrix grains and the precipitates were characterized by transmission electron microscopy (TEM). Thin TEM-lamellae were prepared by Ar-ion milling with special care taken to avoid heating (and possible transformation) of the samples during preparation. TEM and energy-disperse X-ray spectroscopy (EDS) examinations were performed in a Titan Themis C2 200 STEM equipped with a four-segment Super-X EDS detector. The corrector for the spherical aberration (Cs) was applied at the imaging part, while no probe-correction was present. Image resolution limit is 0.08 nm in phase-contrast HRTEM mode, while resolution is 0.16 nm in STEM Z-contrast imaging mode (recorded with a Fischione high-angle annular dark-field (HAADF) detector). HRTEM images were recorded at 200 keV with a 4k × 4k CETA 16 CMOS camera.

EDS data were recorded (together with the HAADF signal) in spectrum-image (SI) mode, where individual X-ray count data can later be post-processed pixel-by-pixel and elemental intensities (and quantified elemental concentrations) can be obtained from any post-selected regions. In that way, distribution of concentrations can be visualized along any lines or over any area.

In the ECAP-processed sample Guinier-Preston (GP) zones, MgZn2 precipitates and a high dislocation density were observed (Figure 1). After aging at 120 °C, coarse MgZn2 precipitates were formed in the grain boundaries, leading to softening, while the dislocation density did not decrease (Figure 2). Annealing at 170 °C yielded a growth of the matrix grains to ~530 nm with a significant decrease of the dislocation density (Figure 3). In addition, GP zones disappeared and MgZn2 precipitates were formed in both the grain interiors and the boundaries. This overaging of the precipitate structure and the decrease of the dislocation density resulted in a lower hardness than after annealing at 120 °C. It was found that the hardness-reduction due to the change of the precipitate structure at 170 °C was higher than that caused by the decrease of the dislocation density.

This research was supported by the Hungarian-Russian Bilateral Research Program (TET) No. 2017-2.3.4-TET-RU-2017-00005 and by grant no. VEKOP-2.3.3-15-2016-00002 of the European Structural and Investment Funds.

![Figure 1: HAADF STEM image illustrating the microstructure of the ECAP-processed sample together with EDS elemental maps for Al, Zn, Mg and Zr obtained on the same area. Zr-rich particles can be distinguished from Zn+Mg-rich particles.](image-url)
Figure 2: HAADF STEM image illustrating the microstructure of the specimen processed by ECAP and then aged at 120 °C together with EDS elemental maps for Al, Zn, Mg and Zr obtained on the same area. MgZr_2 decorate the grain boundaries.

Figure 3: HAADF STEM image illustrating the microstructure of the specimen processed by ECAP and then aged at 170 °C for 2 h with EDS elemental maps for Al, Zn, Mg and Zr obtained on the same area. Flat, hexagonal MgZr_2 precipitates are seen.
Wear Mechanism of Spark Plasma Sintered Multiwall Carbon Nanotubes Reinforced Zirconia Composites Under Dry Sliding Conditions

S. Lamnini (PhD student), K. Balázsi (supervisor), C. Balázsi (supervisor)

Multiwall carbon nanotubes (MWCNTs) reinforced ceramics matrix served not only as enhancing factor of the mechanical properties, but also enabled the formation of an intrinsic solid lubricant effect, thus affording low friction response and remarkable wear resistance. However, controversial results have been often reported with different concentrations. In this work, multiwall carbon nanotubes (MWCNTs) reinforced 8 mol. % yttria-stabilized zirconia (8YSZ) composites were synthesized using ball milling and spark plasma sintering (SPS, at 1400 °C) in different compositions (0, 1, 5, 10 wt. % MWCNTs). The aim of our investigation is to provide an explicit understanding of the wear mechanism features evaluated after friction-test against Si₃N₄ balls used as a counterpart, which can contribute largely to avoid the easier mechanical failure. Furthermore, the effect of sliding speed namely at low (V₁= 0.036 m/s) and high (V₂= 0.11 m/s) was also highlighted (Figure 1). In fact, an outstanding wear improvement at low sliding speed (V₁) was reported with the addition of 1 wt. % of MWCNTs. This was most likely attributed to two main reasons: 1) the formation of a perfectly continuous and uniform tribo-film, 2) the improved flexural strength, fracture toughness and density. Based on Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS) results, we have concluded that the applied sliding speed, grain size / geometry, surface roughness, MWCNTs content and its dispersion into the matrix, altogether plays a vital role to beneficially or adversely influence the tribological performance of the composites.

![Figure 1: Comparative graph presenting the Average Friction Coefficient (μ) during transitory state (0-40m) and steady state (40-400m) for all the composites tested at fix normal load (5N) and different sliding rates (V₁=0.036 m/s, V₂=0.11 m/s)](image-url)
EXAMINATION OF MILLED HEXAGONAL BORON NITRIDE ADDITION ON SINTERED Si₃N₄-H-BN CERAMIC COMPOSITES

(FLAG.ERA “Ceranea” NN127723)

K. Balážsi, M. Furkó, Zs. Fogarassy, C. Balážsi

Silicon nitride (Si₃N₄) ceramics containing 1 and 5 wt.% of hexagonal boron nitride (h-BN) have been prepared by attrition milling and hot-isostatic pressing using three different milling conditions. Thorough morphological characterizations have been carried out to reveal the influence of the milling parameters on the size of the h-BN additives. The results confirmed significant decrease in h-BN particle size by increasing milling time. The transmission electron microscopy (TEM) observations revealed that the h-BN particles were evenly incorporated into the ceramic matrix (Figure 1). Moreover, the increase of the h-BN content decreased significantly the hardness of materials and the hardness values were higher when the size of h-BN was larger (Figure 2).

Figure 1: Bright-field (BF) TEM images of B1/5 (a) C2/1 (b) and D3/1 (c) samples as well as selected area electron diffraction (SAED) on one h-BN platelet within the B1/5 sample (d)

Figure 2: Hardness measurement on Si₃N₄-h-BN composite samples containing 1 and 5 wt.% h-BN additives prepared with different methods. B1/1 and B1/1 samples: h-BN added without pre-milling, C2/1 and C2/5 samples: h-BN added 30 minutes before the milling, D3/1 and D3/5 samples: h-BN added at the beginning of the milling
CO₂ REFORMING OF METHANE BY Ni–In/SiO₂ CATALYST WITH NO COKE FORMATION

J. Károlyi, M. Németh, C. Evangelisti, G. Sáfrán (MFA), Z. Schay, A. Horváth, F. Somodi

The current opinion is that the reduction of carbon dioxide with methane (dry reforming of methane (DRM) CO₂ + CH₄ = 2CO + 2 H₂) would be a suitable reaction, since the product is synthesis gas, which is one of the most important feedstock of chemical industry [1-3]. Unfortunately, carbon deposits more readily form on nickel than on noble metal surfaces during the reaction leading to fast deactivation of the catalyst. Potential catalysts for CO₂ - methane dry reforming were tested in a cooperation of MTA EK Surface Chemistry and Catalysis Laboratory and CNR, Institute of Molecular Science and Technologies Milano [4]. It was shown that the presence of 2 wt% indium on the surface of a 3 wt%Ni/SiO₂ catalyst prevented coke formation during dry reforming of methane.

In efforts to understand the mechanism, TPR revealed that indium was unstable against sintering without nickel on the silica surface, however in the bimetallic catalyst it was in metallic state and mixed with nickel after reduction at 700 °C. The presence of indium profoundly changed the adsorption properties of nickel, as CO-TPD (Temperature Programmed Desorption) measurements suggested. XPS measurements showed changes in the electronic structure of nickel on the Ni–In/SiO₂ catalyst after reduction, moreover, they revealed the presence of bimetallic particles which surface composition found to be Ni₂In, lower than the expected Ni₃In, referring to indium enrichment on the surface.

Table 1: Hydrogen consumption during TPR and the average particle size and dispersion of nickel calculated based on the results of CO pulse chemisorption

<table>
<thead>
<tr>
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<th>3 wt% Ni/SiO₂</th>
<th>3 wt% Ni–2 wt% In/SiO₂</th>
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<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
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<tr>
<td>H₂ (cm³ /g) a</td>
<td>9.8</td>
<td>10.3</td>
</tr>
<tr>
<td>CO (cm³ /g)</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>D (%) b</td>
<td>4.3</td>
<td>7.1</td>
</tr>
<tr>
<td>d (nm) b</td>
<td>23.4</td>
<td>14.3</td>
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aValues at standard temperature and pressure (22414 cm³ / mol).
bValues calculated from the amount of chemisorbed CO.

Simultaneously, HRTEM analysis of the bimetallic catalyst showed the presence of NiIn and Ni₃In alloy nanoparticles. TEM analysis of the spent catalysts after 24h time on stream showed that the average particle size of the bimetallic catalyst was slightly smaller than that of the monometallic catalyst.

Based on the present results, the higher catalytic activity and outstanding carbon tolerance of the bimetallic Ni–In/SiO₂ catalyst is the consequence of a structural and electronic effects of indium.

Related publications


THINNING OF TEM SAMPLES (KNOW-HOW)

Gy. Sáfrán, N. Szász

Introduction

Conventional preparation of TEM samples in MTA EK MFA is carried out by Ar-ion beam thinning so that the sample is mounted on the holder by carbon paste. Carbon contamination of samples is a severe problem when working with new generation C₄-corrected Transmission Electron Microscopes (TEM). High intensity beam in HRTEM and STEM modes may, unfortunately, deposit artefacts of cracking products from the migrating residue of the carbon paste. The deposited contamination raises difficulties or balks the TEM investigation. Fixing the sample with carbon paste is difficult and time consuming. Furthermore, it is risky, since during its removal the sample may be spoiled with the dissolved carbon paste. Consequently, using carbon paste is disadvantageous from the point of view of both preparation and TEM study of the samples! The installation of the C₄-corrected TEM “THEMIS” in the Thin Films Physics Laboratory arise the need to further develop our thinning technology and to skip carbon paste.

New technology and sample holder design

In order to replace carbon paste used earlier for mounting the samples a new sample holder (Figure 1) has been constructed that implements mechanical fixing of the sample. In addition, with carbon-free technology in mind, we changed the composition of glue that embeds the slabs of samples into the Ti disk: instead of Araldite mixed with carbon powder we use Gatan G1 with alumina or Ti-powder (Figure 2).

Results

The new mechanical construction, together with the new composition of embedding glue, was tested in our lab during daily TEM sample preparations over the year 2018. It showed, undoubtedly, that the new solution provides reliable, clean, mounting of samples, good heat conductance, small access angle of ion beam, backlight illumination- and centring possibility. Besides, it is simple and cheap, easy to manufacture, and compatible with all variations of sample holders from IV 3 till IV7.

Exploitation of know how

Beside daily utilization in the Thin Films Physics Laboratory the know-how of the new construction has been sold for 3M Ft to TECHNOORG LINDA, manufacturer of our ion beam thinning equipment’s.
Micro-combinatorial Analysis of Concentration Dependent Properties of Binary Films

G. Sáfrán, T. Lohner, B. Kalas, P. Petrik, Zs. Zolnai, M. Serényi, M. Fried, G. Dobrik, J. Gubicza (ELTE), N.Q. Chinh (ELTE)

A “one sample concept” combinatorial method has been worked out and patented for an efficient TEM study of concentration dependent properties of binary films [1,2]. The new technique called “µ-combinatory” has been adapted to further analytical measurements e.g. AES, XRD, RBS, ellipsometry, nanoindentation. Contrary to traditional “multiple sample combinatorial techniques” we synthetize a single sample of suitable size that exhibits a concentration gradient and includes all compositions of a binary system. The µ-combinatorial sample for TEM appears as a thin gradient film on a 3mm diameter TEM grid, while for other analytical measurements the gradient sample is deposited on a 25x10 mm² wafer. That permits a very efficient, even automated, analysis of the microstructure, physical and chemical properties and the collection of complete data libraries within a single measuring session. A major technical progress in 2018 was that the manual control has been replaced by a processor unit controlling both power of DC magnetrons and synchronized movement of the mechanics.

The efficiency of the method is demonstrated by achievements as below.

**AlMg system:** In a cooperation with N.Q. Chinh (ELTE) TEM and nano-hardness studies of the AlMg system were carried out in the technologically relevant range of 0-30 Mg%. Figure 1 shows the microstructure revealed by TEM and SAED of MgAl at 1%, 10% and 30% Mg content indicating that Mg addition radically decreases grain size. Pure Al layer shows fcc Al phase with large grains of typically 60-120nm. By adding 1wt% Mg the grain size decreases to 30-100nm. Up to about 10% Mg the fcc Al(Mg) solid solution phase is present exhibiting 20-40nm grains. At 25% Mg and above (30%), however, a very fine grained Al<sub>3</sub>Mg<sub>2</sub> phase appears beside the still existing fcc Al(Mg) that shows 10-20 nm size grains (Figure 1).

Nanoindentation measurements pointed out that 1% Mg content increases hardness to 3-times of that of Al, followed by monotonous increase to a saturation of 4.5-times of Al at 20% Mg.

**SiGe system:** TEM, RBS, and ellipsometry investigations were carried out, together with researchers of the Photonics Laboratory, on non-hydrogenated µ-combinatorial SiGe samples. The concentration diagrams, depicted in Figure 2, measured by RBS and EDS along the length of the 25x10mm² size µ-combinatorial sample show linear change with the position. The full range concentration dependence of refractive index n and absorption k of a-SiGe (Figure 3) was determined and plotted in a color-coded map by ellipsometry in the λ=400-1600 nm wavelengths range [3,4]. The extracted diagrams show Vegard’s low-like, linear dependence of n and k on composition. Similarly, XRD measurements (by J. Gubicza, ELTE) of SiGe layers crystallized by annealing also showed Vegard’s low-like, linear dependence of lattice parameter on composition.
Figure 2: Concentration diagrams measured along the gradient of a µ-combinatorial SiGe sample (25x10mm$^2$ size) by RBS (continuous) and EDS (- - -), respectively.

Figure 3: Color-coded maps of refractive index $n$ and absorption $k$ of a-SiGe as a function of composition at wavelengths of $\lambda=400$-1600 nm. Top: cleared diagrams of $n$ and $k$ at $\lambda=849.7$ nm. (Positions of -1, 0 and 1 cm correspond to Si$_{1-x}$Ge$_x$ = 1, 0.5 and 0, respectively.)

Related publications


[5] Hungarian Development and Innovation Operative Program GINOP-2.1.7-15-2016-02073 The development of the µ-combinatorial method and device is done in a co-operation of MTA EK MFA and Holocom
DEVELOPMENT AND CHARACTERIZATION OF MULTI-ELEMENT DOPED HYDROXYAPATITE COATINGS ON METALLIC IMPLANT MATERIALS

M. Furkó (PhD student), C. Balázsi (supervisor)

The aim of this research work is to develop coatings onto implant materials which possess both antimicrobial and biocompatible properties. Coatings were prepared by pulse current deposition technique. The pure hydroxyapatite (HAp) layer was doped and co-deposited with Ag\(^{+}\), Zn\(^{2+}\), Mg\(^{2+}\) and Sr\(^{2+}\) ions (Figure 1). The corrosion and biodegradable properties of layers were studied by carrying out electrochemical impedance spectroscopy measurements in simulated body fluid (SBF) using three-electrode open cell over a long time period. The biocompatible characteristics of layers were investigated by seeding osteoblast-like MG-63 cells onto the samples’ surface. The most corrosion rate of coating increase with immersion time, which proves its biodegradable property (Figure 2).

Figure 1: The elemental map of the composition of multi-element doped HAp (reference - silver, Ca - orange, P - blue, Ti – dark blue, Ag - yellow, Zn - red, Sr - purple, Mg - green)

Figure 2: Nyquist diagrams of multi-element doped HAp coated Ti6Al4V alloy. The curves were recorded several times over a two-week period in SBF solution at 37 °C.
CERAMIC DISPERSED AUSTENITIC STRENGTHENED STEELS

H. R. Ben Zine (PhD student), F. Cinar Sahin (ITU Istanbul), Zs. Czigány, K. Balázsi (supervisor), C. Balázsi (supervisor)

In this work, the 316L austenitic strengthened stainless steel based composites were developed by powder technology. Attrition milling and sintering were used for production of Ceramic Dispersed Austenitic Strengthened Steels (CDSS) with 0.33 wt% and 1 wt% nanosized SiC addition. The highly efficient attrition milling provided an efficient size reduction of the 316L steel grains and homogeneous distribution of the ceramic nanoparticles before sintering process. Spark plasma sintering (SPS) was used for fast compaction of milled powder mixtures. The density of composites decreased with increasing the amount of SiC due to its lower density. The SiC addition improved the hardness of the 316L, the 316L/1 wt% SiC shows lower hardness compared to the 316L/0.33 wt% SiC composite due to its lower density. A simultaneous transgranular and intergranular fracture behaviour (Figure 1) have been observed after the 3 points bending test of the 316L/1wt% SiC composite where an average bending strength high as 1127.4 MPa has been recorded at room temperature. In the case of the 316L/0.33wt% SiC the samples were just bended due to their higher ductility. Tribological properties of the sintered composites have been studied, and it was observed that the addition of the SiC improves the tribological properties of the 316L stainless steel. Friction coefficients of 0.962, 0.879 and 0.930 have been measured, respectively, for all of the sintered reference sample 316L, 316L/0.33 wt% SiC and the 316L/1wt% SiC composites. The investigation of the sintered composites by TEM confirmed the distribution of the ceramic particles to the grains boundaries (Figure 2).
NEW APPROACHES IN THE DEVELOPMENT OF HYPOALLERGENIC IMPLANT MATERIAL IN ORTHOPAEDICS: STEPS TO PERSONALISED MEDICINE

(EU FP7 “HypOrth”)

K. Balázi, Zs. Fogarassy, V. Varga, T. Zagyva, D. Delfonse (Mathys, Switzerland), C. Lohman (Magdeburg Un., Germany), J. Lorenzen (Teknologisk Institute, Denmark), C. Balázi

Conventional materials of endoprostheses, such as Metal-on-Metal (MoM) are not suitable for all people, as some individuals develop adverse immune reactions to the constituents of metal alloys. The process, which leads to this adverse immune reaction and why some individuals react to the implanted materials whereas others do not, are not yet understood. The main aspect of our project was the development of the novel material combination for endoprostheses with excellent hypoallergenic and antibacterial properties. This new biomaterial was developed from raw waste biogenic materials as seashells using combination of the powder technology with novel electrodeposition method – electrospraying.

Nanosized bioactive powder from seashells was prepared by highly efficient attritor milling. Electrospraying was used as a coating technology for the bioceramics film deposition (Figure 1). We confirmed that these coatings contained important trace elements as strontium or magnesium which increased the osteointegration activity. Moreover, the seashell derived coating (TAV TPS HAS (titanium-aluminium-vanadium/plasma-sprayed titanium/hydroxyapatite)) exhibited the highest biocompatibility among the examined coatings (Figure 2). We also confirmed that the properties of coatings after sterilization were similar from the point of view of structure, adhesion and biocompatibility to starting as-received bioactive coatings. The detailed steps of preparation and characterization are confidential. The project was successfully accomplished and the final report was accepted by EU Commission.
Graphene-ceramic Composites for Tribological Application in Aqueous Environments

(OTKA M-ERANET “Grace”)

C. Balážsi, Zs. Fogarassy, V. Varga, M. Knoch (FCT), J. Dusza (IMR SAS, Slovakia), A. Kailer (IMW Franhoufer, Germany), K. Balážsi

The M-ERANET „Grace” project was oriented to the development of advanced Si$_3$N$_4$/graphene and SiC/graphene ceramic composites. There is a strongly growing demand for highly wear resistant and reliable ceramic materials that may be widely used in industrial applications and energy production. Special attention is paid to components that are used under severe conditions and only lubricated by the surrounding media that are mainly aqueous. Reliability and efficiency of these components need to be improved by using high performance ceramics with superior tribological and mechanical properties.

Recent basic research of the project partners on the development of graphene containing ceramic composites showed that the realization of the nanocomposites with remarkably increased wear resistance and fracture toughness was possible. Multi-layered graphene (MLG) was prepared by attritor milling at 10 h intensive milling of few micrometre sized graphite powders. The large quantity, low cost and quick preparation process are main strengths of our MLG. Si$_3$N$_4$/MLG nanocomposites were prepared by attritor milling and sintered by hot pressing (HP). The Si$_3$N$_4$ ceramics were produced with 1 wt%, 3 wt%, 5 wt% and 10 wt% content of MLG. The tribological behaviour of composites in aqueous environment was investigated (Figure 1). This study showed decrease of wear at increased MLG content (Figure 2).

![Figure 1: Friction property of Si3N4 / MLG composites with different MLG content.](image1)

![Figure 2: Wear of composites as function of MLG content.](image2)

Our current knowledge in the field of ceramic nanocomposites shows that is possible to make ceramic materials by incorporating graphene into the Si$_3$N$_4$ and SiC structure. The new approach is very promising, since ceramic microstructures can be designed with high toughness and provide improved wear resistance at low friction.
BACTERIA REPELLENT LAYER MADE OF FLAGELLIN

("Lendület" grant LP2012-26/2012 of HAS, ERC_HU, BIONANO GINOP-2.3.2-15-2016-00017, OTKA grant NN117849)

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The development of bacteria repellent surface coatings is critical in various fields ranging from biosensing to health care, biotechnology and food production. In the present study we exploit that the protein flagellin rapidly forms a dense and oriented monolayer on hydrophobic surfaces upon adsorption from aqueous solution. This oriented layer mimics the surface of bacterial flagellar filaments and has excellent bacteria repellent properties. In situ OWLS (Optical Waveguide Lightmode Spectroscopy) measurements were used to monitor online both the formation of the protein layer on the silanized sensor surface and subsequent bacterial adhesion (see Fig. 1). The adhered cells were also visualized by fluorescent microscopy and the formed protein film was characterized by AFM (Atomic Force Microscopy). In parallel control experiments, the adherence of bacteria was measured on bare hydrophobic surfaces as well. Both OWLS and microscopy results well confirmed that the flagellin coating drastically reduced the adhesion of E. coli cells. Therefore, a novel type of bacteria repellent layer made of flagellin is demonstrated [1].

Figure 1: Schematic representation of the differences between the bacterial adhesion on the flagellin coated and on the uncoated hydrophobic surface

Related publication

KINETICS AND STRUCTURE OF SELF-ASSEMBLED FLAGELLIN MONOLAYERS ON HYDROPHOBIC SURFACES IN THE PRESENCE OF HOFMEISTER SALTS: EXPERIMENTAL MEASUREMENT OF THE PROTEIN INTERFACIAL TENSION AT THE NANOMETER SCALE

(“Lendület” grant LP2012-26/2012 of HAS, ERC_HU, KH-17, NKFI-6, K-124932, BIONANO_GINOP-2.3.2-15-2016-00017, OTKA grant NN117849)

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Flagellins (building blocks of bacterial flagellar filaments) do not preferentially adsorb on hydrophilic substrates, but very rapidly forms an oriented, dense and stable monolayer on hydrophobic surfaces, where the hypervariable D3 domain (one of the four flagellin domains) is oriented toward the solution. It presents a repellent surface coating to bacteria or cancer cells, thus this property can be utilized in biosensors and biofunctionalized surfaces. In this work, we monitored the adsorption-desorption layer structure of the bacterial protein flagellin in the presence of Hofmeister salts by a surface sensitive label-free optical biosensor (optical waveguide lightmode spectroscopy, OWLS). The recorded OWLS data were analysed by a computer code using a set of coupled differential equations modelling the adsorption-desorption process. By supposing reversibly and irreversibly adsorbed protein states with different adsorption footprints, the kinetic data could be perfectly fitted. We revealed that the proteins adsorbing in the presence of kosmotropic salts had smaller footprints, leading to a more oriented and densely packed layer. Kosmotropic salts increased both the adsorption rate constant and the transition rate constants from the reversibly to the irreversibly adsorbed state (see Fig. 1). In contrast, chaotropic salts increased the desorption rate constant and led to decreased adsorbed mass and a more loosely packed film. Neither circular dichroism spectroscopy in bulk solutions or Fourier transform infrared spectroscopy of surface-adsorbed flagellins could reveal significant structural changes due to the presence of the Hofmeister salts, and supported our conclusions about the adsorption mechanism. On the basis of the measured kinetic and structural data (footprints of adsorbed proteins), we developed a model to calculate the protein-water-substrate interfacial tension in the presence of Hofmeister salts, and compared the experimentally obtained values with related literature data. The calculated values are consistent with previously published data of surface tension changes, and—to the best of our knowledge—represent the first experimental results for this quantity [1].

Figure 1: Schematic illustration of the adsorption kinetics of flagellin proteins on a hydrophobic surface

Related publication

INTERACTION OF POSITIVELY CHARGED GOLD NANOPARTICLES WITH CANCER CELLS MONITORED BY AN IN SITU LABEL-FREE OPTICAL BIOSensor AND TRANSMISSION ELECTRON MICROSCOPY

(“Lendület” grant LP2012-26/2012 of HAS, ERC_HU, KH-17, MedinProt)

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Functionalized nanoparticles (NPs) can penetrate into living cells and vesicles, opening up an extensive range of novel directions. For example, NPs are intensively employed in targeted drug delivery and biomedical imaging. However, the real-time kinetics and dynamics of NP–living cell interactions remained uncovered. In this study, we in situ monitored the cellular uptake of gold NPs –functionalized with positively charged alkaline thiol– into surface-adhered cancer cells, by using a high-throughput label-free optical biosensor employing resonant waveguide gratings. The characteristic kinetic curves upon NP exposure of cell-coated biosensor surfaces were recorded and compared to the kinetics of NP adsorption onto bare sensor surfaces. We demonstrated that from the above kinetic information, one can conclude about the interactions between the living cells and the NPs (see Fig. 1). Real-time biosensor data suggested the cellular uptake of the functionalized NPs by an active process. It was found that positively charged particles penetrate into the cells more effectively than negatively charged control particles, and the optimal size for the cellular uptake of the positively charged particles is around 5 nm. These conclusions were obtained in a cost-effective, fast, and high-throughput manner. The fate of the NPs was further revealed by electron microscopy on NP-exposed and subsequently fixed cells, well confirming the results obtained by the biosensor. Moreover, an ultrastructural study demonstrated the involvement of the endosomal–lysosomal system in the uptake of functionalized NPs and suggested the type of the internalization pathway. NPs may act as model systems to imitate host cell-bacteria interactions and penetration in biosensor measurements. Furthermore, these measurement settings and results can be applied to study the uptake of NPs by bacteria as well [1].

Figure 1: Schematic illustration of the concept of evanescent label-free biosensors in NP uptake detection

Related publication

**HIGH-RESOLUTION ADHESION KINETICS OF EGCG-EXPOSED TUMOR CELLS ON BIOMIMETIC INTERFACES: COMPARATIVE MONITORING OF CELL VIABILITY USING LABEL-FREE BIOSENSOR AND CLASSIC END-POINT ASSAYS**

(“Lendület” grant LP2012-26/2012 of HAS, ERC_HU, KH-17, OTKA grant 104275)

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A high-throughput label-free resonant waveguide grating biosensor, the Epic BenchTop (Epic BT) was utilized to in situ monitor the adhesion process of cancer cells on Arg-Gly-Asp tripeptide (RGD) displaying biomimetic polymer surfaces. Using highly adherent human cervical adenocarcinoma (HeLa) cells as a model system, cell adhesion kinetic data with outstanding temporal resolution were obtained. We found that pre-exposing the cells to various concentrations of the main extract of green tea, the (−)-epigallocatechin gallate (EGCG), largely affected the temporal evolution of the adhesion process. For unexposed and low dosed cells, sigmoid shaped spreading kinetics was recorded. Higher dose of EGCG resulted in a complete absence of the sigmoidal character, and displayed adsorption-like kinetics. By using the first derivatives of the kinetic curves, a simple model was developed to quantify the sigmoidal character and the transition from sigmoidal to adsorption-like kinetics (see Fig. 1). The calculations showed that the transition happened at EGCG concentration of around 60 µg/mL. Using the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide end-point assay, we concluded that EGCG is cytotatic but not cytotoxic. The effect of EGCG was also characterized by flow cytometry. We concluded that, using the introduced label-free methodology, the shape of the cell adhesion kinetic curves can be used to quantify in vitro cell viability in a fast, cost-effective, and highly sensitive manner [1]. This method probably can be used with bacterial cells as well to demonstrate the antibacterial effects of certain further natural compounds.

**Figure 1: Schematic illustration of the working principle of the Epic BT biosensor and the steps of the measurement (left). In case of adsorption kinetic curve, the cell attaches but does not adhere onto the biosensor surface. This phenomenon indicates a nonliving, “dead” process. Note, it also occurs when proteins adsorb onto the surface. In case of sigmoidal kinetic curve, the cells adhere onto the biosensor surface. This phenomenon indicates a “living” process.**

**Related publication**

LABEL-FREE OPTICAL BIOSNSOR FOR REAL-TIME MONITORING THE CYTOTOXICITY OF XENOBIOTICS: A PROOF OF PRINCIPLE STUDY ON GLYPHOSATE

("Lendület" grant LP2012-26/2012 of HAS, ERC_HU, OTKA grant K109865)

E. Farkas, A. Szekacs (Agro-Environmental Research Institute, Budapest), B. Kovacs, M. Olah (Agro-Environmental Research Institute, Budapest), R. Horvath, I. Szekacs

Rapid and inexpensive biosensor technologies allowing real-time analysis of biomolecular and cellular events have become the basis of next-generation cell-based screening techniques. Our work opens up novel opportunities in the application of the high-throughput label-free Epic BenchTop optical biosensor in cell toxicity studies. The Epic technology records integrated cellular responses about changes in cell morphology and dynamic mass redistribution of cellular contents at the 100–150 nm layer above the sensor surface. The aim of the present study was to apply this novel technology to identify the effect of the herbicide Roundup Classic, its co-formulant polyethoxylated tallow amine (POEA), and its active ingredient glyphosate, on MC3T3-E1 cells adhered on the biosensor surface (see Fig.1). The half maximal inhibitory concentrations of Roundup Classic, POEA and glyphosate upon 1 h of exposure were found to be 0.024%, 0.021% and 0.163% in serum-containing medium and 0.028%, 0.019% and 0.538% in serum-free conditions, respectively (at concentrations equivalent to the diluted Roundup solution). These results showed a good correlation with parallel end-point assays, demonstrating the outstanding utility of the Epic technique in cytotoxicity screening, allowing not only high-throughput, real-time detection, but also reduced assay run time and cytotoxicity assessment at end-points far before cell death would occur [1].

Figure 1: Schematic representation of the measurement and data evaluation methodology

Related publication

INTEGRIN TARGETING OF GLYPHOSATE AND ITS CELL ADHESION MODULATION EFFECTS ON OSTEObLASTIC MC3T3-E1 CELLS REVEALED BY LABEL-FREE OPTICAL BIOSENSING

(“Lendület” grant LP2012-26/2012 of HAS, ERC_HU, KH-17, NVKP_16-1-2016-0049, OTKA grant K109865)

I. Szekacs, E. Farkas, B.L. Gemes (Agro-Environmental Research Institute, Budapest), E. Takacs (Agro-Environmental Research Institute, Budapest), A. Szekacs (Agro-Environmental Research Institute, Budapest), R. Horvath

Cell adhesion is the crucial event in numerous physiological and pathophysiological processes. Foreign substances can affect cellular processes through receptors, ion channels, enzymes, binding proteins or the cytoskeleton. Biosensor techniques and their application in different areas, including cytotoxicology, is becoming of growing significance. Whole cell-based sensors gain utmost importance due to their capability to measure comprehensive and functional effects of different xenobiotics.

An evanescent filed based surface-sensitive resonant waveguide grating (RWG) biosensor was applied for high-throughput label-free detection of impacts of the world leading herbicide active ingredient glyphosate on cell adhesion in real time and quantitative evaluation. In the present study we discovered and thoroughly examined a new, yet unidentified, properties of glyphosate as cell adhesion modulator. The RWG technique was employed for measuring kinetics of cell adhesion to glyphosate adsorbed on biosensor surfaces and by measuring the antagonistic action of glyphosate on cell binding to Arg-Gly-Asp (RGD)-displaying polymer surfaces (see Fig. 1). The results obtained demonstrate that living preosteoblastic cells can adhere to glyphosate adsorbed on the sensor surface, showing ligand-specific kinetics. Soluble glyphosate significantly reduces cell adhesion via blocking RGD-specific integrins in a concentration-dependent manner, as also validated by competitive binding assays to recombinant receptor αvβ3 in both enzyme-linked immunosorbent assay (ELISA) and biosensor formats. Using this novel methodology, the half maximal inhibitory concentration (IC50) for glyphosate in living osteoblastic cells was determined to be 20.6 mM. The affinity of glyphosate to cell adhesion receptors is also determined. The introduced methodology is fast, sensitive, and biological effects were revealed using intact, living cells [1].

Figure 1: Schematic illustration of the working principle of the cell-based biosensor and the concentration-dependent effects of glyphosate on cell adhesion. (a) MC3T3-E1 cells spread on a sensor surface treated with 0.1% glyphosate solution. (b) Inhibition of cell adhesion by glyphosate at 0.2–1.7% concentration in the solution (with complete blockage achieved at 1.7%). (c) Prevention of cell adhesion onto PP:PPR surface by preincubation of the cells with glyphosate at 0.47% concentration in the solution. (d) Detaching MC3T3-E1 cells adhered to a surface modified with PP:PPR by glyphosate at 0.9% concentration in solution.

Related publication

**In situ Viscoelastic Properties and Chain Conformations of Heavily Hydrated Carboxymethyl Dextran Layers: A Comparative Study Using OWLS and QCM-I Chips Coated With Waveguide Material**

("Lendiület" grant LP2012-26/2012 of MTA, ERC_HU, KH-17)


Hydration, viscoelastic properties and dominant structure of thin polymer layers on the surface of waveguide material were evaluated using optical waveguide lightmode spectroscopy (OWLS) and quartz crystal microbalance (QCM) methods. The fundamentally different principles of the two applied label-free biosensors enable to examine analyte layers from complementary aspects, e.g. to determine the amount of bound water in hydrated layers. In this study, a new QCM instrument with impedance measurement (QCM-I) was introduced. Its specially designed sensor chips, covered by thin film of waveguide material (SiO$_2$-TiO$_2$), supply identical surface as used in OWLS sensors, thus enabling to perform parallel measurements on the same type of surface. Viscoelastic analysis of the measured data was performed by our evaluation code developed in MATLAB environment, using the Voinova’s Voigt-based model. *In situ* deposition experiments on the ultrathin films of poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG) were conducted for instrumental and code validation. Additionally, a novel OWLS-QCM data evaluation methodology has been developed based on the concept of combining hydration and viscoelastic data with optical anisotropy results from OWLS measurements (see Fig. 1). This methodology provided insight into the time-dependent chain conformation of heavily hydrated nano-scaled layers, resulting in unprecedented structural, hydration and viscoelastic information on covalently grafted ultrathin carboxymethyl dextran (CMD) films, which are basically antifouling coatings that can be specifically conjugated by adhesive motifs in order to arrange cells and bacteria on biosensor surfaces. The measured mass values as well as hydration and viscoelastic properties were compared with the characteristics of PLL-*g*-PEG layers [1].

![Figure 1: Schematic representation of the measurement and data evaluation methodology developed and applied in this work](image)

**Related publication**

COMPETITION AND PARTNERSHIP BETWEEN CONFORMITY AND PAYOFF-BASED IMITATIONS IN SOCIAL DILEMMAS

(OTKA K120785)

A. Szolnoki and X. Chen

Learning from a partner who collects a higher payoff is a frequently used working hypothesis in evolutionary game theory. One of the alternative dynamical rules is when the focal player prefers to follow the strategy choice of the majority in the local neighbourhood, which is often called a conformity-driven strategy update. In this work we assumed that both strategy learning methods are present and compete for space within the framework of a coevolutionary model.

We have shown that there are parameter regions, like strong snowdrift game situations at high temptation ($T$) or high sucker’s payoff ($S$) values where the competition of different learning methods results in the unambiguous victor of payoff-driven strategy learning. Here the role separating cooperator-defector pairs provide so high collective payoff value that cannot be beaten by a homogeneous domain which would be a consequence of a conformity-driven learning method.

![Figure 1](image-url)

Figure 1: Phase diagram of snowdrift game where payoff-driven and conformity-driven strategy learning protocols are competing for space. Full C (full D) label marks the parameter regions where only co-operator (defector) strategies survive in the stationary state. ‘Payoff-driven’ label marks the region where payoff-driven strategy learning protocol prevails and related cooperator and defector players form a stable winning solution. The phase denoted by ‘mixed’ label shows where all learning protocols and all strategies coexist. For comparison, green dotted line marks the border of full cooperator state when only payoff-driven learning protocol is available for players in a uniform system.

Nevertheless, for less sharp snowdrift game regions at smaller $T$ and $S$ values the coevolution of different learning methods is useful to reach a full cooperative state that would not be reachable otherwise. In the latter case the homogeneous cooperator domains can invade the whole space by enjoying the advantage of conformity-driven learning method. Interestingly, in the stag-hunt game region the simultaneous presence of different learning methods reveals a novel way of collaboration that cannot be observed otherwise. Here conformity-driven cooperators can resist the invasion of payoff-driven defectors and neighbouring payoff-driven cooperators can attack conformity-driven defectors successfully. The expected symmetry is broken for defectors because conformity-driven ($o_D$) and payoff-driven ($p_D$) states cannot form similarly efficient alliance. In this way the active partnership of different types of cooperator players allows them to extend the full cooperator state to those parameter values which belonged to the sovereignty of defectors in the classic payoff-driven model.
Figure 2: Spatial evolution of the four competing states in a 400×400 system at $T=1.4$ and $S=0.4$ where the simulation is launched from a prepared patch-like initial state where all kind of interfaces between competing players can be found. In this way we can monitor all emerging pattern formations simultaneously via a single run. Here dark (light) blue denotes payoff-driven (conformity-driven) cooperators, while dark (light) red marks payoff-driven (conformity-driven) defectors, as it is marked by white labels in panel (a). This panel represents the early stage of evolutionary process after 20 MCSs. Further stages of the evolutionary process are shown at 50, 150, 250, 350, and 800 MCSs. Finally, the system evolves into a homogeneous oC state (not shown). The circles and ellipses highlight the specific invasion fronts between different types of domains.

Related publication

Griffiths phases (GPs), generated by the heterogeneities on modular networks, have recently been suggested to provide a mechanism, rid of fine parameter tuning, to explain the critical behaviour of complex systems. One conjectured requirement for systems with modular structures was that the network of modules must be hierarchically organized and possess finite dimension. We investigate the dynamical behaviour of an activity spreading model, evolving on heterogeneous random networks with highly modular structure and organized non-hierarchically. We observe that loosely coupled modules act as effective rare-regions, slowing down the extinction of activation. As a consequence, we find extended control parameter regions with continuously changing dynamical exponents for single network realizations, preserved after finite size analyses, as in a real GP. The avalanche size distributions of spreading events exhibit robust power-law tails. Our findings relax the requirement of hierarchical organization of the modular structure, which can help to rationalize the criticality of modular systems in the framework of GPs.

Related publication

Correlation Analysis ofJointly Propagating Genetic and Musical Characteristics of Modern and Ancient Populations in Eurasia and America – A Simultaneous Quest for Ancient Human Populations and Their Musical Parent Languages

Z. Juhász, H. Pamjav et al.

In this study, we aimed to illustrate the efficiency of correlation analysis of musical and genetic characteristics in research for certain common ethnic and ethno-musical roots of the mankind. The comparison of the results to archaeogenetic data shows that correlations of recent musical and genetic data may reveal past cultural and migration processes resulting in recent connections. (Accepted for publication in Molecular Genetics and Genomics.)

Figure 1: al distribution of the common mean weight vectors derived from similar rank lists of the populations studied, belonging to the musical types and haplogroups indicated in the right upper part. The result refers to an association of haplogroups X, U*, U2, HV*, T, K, J and H, as well as melody types of descending melody contours and high ranges. The highest weights of this association of genetic and musical types are found in Anatolia, the Carpathian Basin, the Caucasus and Sicily. The given haplogroup association was compared to ancient archaeogenetic samples, and it was found to be dominant in Neolithic farmer populations in the Fertile Crescent, so the corresponding association of melody types may be attributed to one of the well-known Neolithic migrations. Four closely related melodies arising from Hungary, the Caucasus-area (Karachay), Anatolia and Sicily verify the existence of this hypothetical musical parent language.
### ABBREVIATIONS

<table>
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<tr>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>1DPC</td>
<td>One-Dimensional Photonic Crystal</td>
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<tr>
<td>AEKI</td>
<td>Institute for Atomic Energy Research</td>
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<td>AER</td>
<td>Atomic Energy Research</td>
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<td>AES</td>
<td>Auger Electron Spectroscopy</td>
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<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<td>ALD</td>
<td>Atomic Layer Deposition</td>
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<td>American Nuclear Society</td>
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<td>ANSI</td>
<td>American National Standards Institute</td>
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<td>AOP</td>
<td>Advanced Oxidation Processes</td>
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<td>ARDM</td>
<td>Automatic Radioactive Material Detection</td>
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<td>Experimental Helium Gas Cooled Fast Reactor Developed by the European V4G4</td>
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<td>ATR IR</td>
<td>Attenuated Total Reflection Infrared Spectroscopy</td>
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<td>New Irradiation Device at the Budapest Research Reactor</td>
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<td>Land Border Crossing Place</td>
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<td>Boron Coated Straw</td>
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<td>BME</td>
<td>Budapest University of Technology and Economics</td>
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<td>BNC</td>
<td>Budapest Neutron Centre</td>
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<td>BrightnESS</td>
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<td>BRR</td>
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<td>BSW</td>
<td>Bloch Surface Wave</td>
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<td>BZN</td>
<td>Bay Zoltán Nonprofit Ltd. for Applied Research</td>
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<td>CAN bus</td>
<td>Controller Area Network</td>
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<td>CATHARE</td>
<td>French Thermohydraulic Code</td>
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<tr>
<td>C-BORD</td>
<td>H-2020 EU Project, effective Container inspection at BORDer control points</td>
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<tr>
<td>CDSS</td>
<td>Ceramic Dispersed Austenitic Strengthened Steel</td>
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<td>CERIC</td>
<td>Central European Research Infrastructure Consortium</td>
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<td>Centre Européen pour la Recherche Nucléaire (French name of the European Organization for Nuclear Research)</td>
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<td>(OAH) Centre for Emergency Response</td>
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<td>CMC</td>
<td>Carboxymethyl-Cellulose</td>
</tr>
<tr>
<td>CMD</td>
<td>Classical Molecular Dynamics, Carboxymethyl-dextran</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary Metal-oxide Semiconductor</td>
</tr>
<tr>
<td>CODEX</td>
<td>Core Degradation Experiment</td>
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<tr>
<td>CONCERT</td>
<td>EU H2020 Project for the Integration of Radiation Protection Research</td>
</tr>
<tr>
<td>CONFIDENCE</td>
<td>Consortia of an European Joint Programme (COoping with uNcertainties For Improved modelling and DEcision making in Nuclear emergenCiEs)</td>
</tr>
<tr>
<td>CRP</td>
<td>IAEA Coordinated Research Project</td>
</tr>
<tr>
<td>CTC</td>
<td>Circulating Tumor Cell</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>D&amp;D</td>
<td>Decommissioning and Dismantling</td>
</tr>
<tr>
<td>D3S</td>
<td>Distributed Space Weather Sensor System</td>
</tr>
</tbody>
</table>
DFT  Density Functional Theory
DGA  Diglycol Amide
DHR  Decay Heat Removal
DICP  Dalian Institute of Chemical Physics, China
DLR  German Aerospace Centre
DLS  Dynamic Light Scattering
DNA  Deoxyribonucleic Acid
DPA  Displacement Per Atom
DRIE  Deep Reactive Ion Etching
DRIFTS  Diffuse Reflectance Fourier Transform Infrared Spectroscopy
DRM  Dry Reforming
DS  Dual Scattering
DSBs  Double Strand Breaks
DSC  Differential Scanning Calorimetry
ECAP  Equal Channel Angular Pressing
ECSS  European Cooperation for Space Standardization
EDM  Electrical Discharge Machining
EDS, EDX  Energy-dispersive X-ray Spectroscopy
EELS  Electron Energy Loss Spectroscopy
EEW  Electric Explosion of Wires
EGCg  Epigallocatechin Gallate
EIS  Electrochemical Impedance Spectroscopy
EMC  Electromagnetic Compatibility
EMR  Electron Magnetic Resonance
ELISA  Enzyme-Linked Immunosorbent Assay
ELTE  Eötvös Loránd University, Budapest
EM  Engineering Model
ENTSO  European Network of Transmission System Operators for Electricity
EPS  Environmental Protection Service
EQM  Engineering Qualification Model
ESA  European Space Agency
ESEO  European Student Earth Orbiter
ESI-MS  Electrospray Ionisation Mass Spectrometry
ESIS  European Structural Integrity Society
ESS  European Spallation Source, Lund
EURDEP  European Radiological Data Exchange Platform
EWE  Electric Wire Explosion
EXAFS  Extended X-ray Absorption Fine Structure
F2R  Flex to Rigid
FA  Fuel Assemblies
FCC  Face Centred Cubic
FEM  Finite Element Method
FESEM  Field Emission Scanning Electron Microscopy
FFT  Fast Fourier Transform
GC  Gas Chromatography
GFR  Gas-Cooled Fast Reactor
GP  Guinier-Preston
GPA  Geometrical Phase Analysis
GPU  Graphics Processing Unit
GPs  Griffiths Phases
GRS  „Gesellschaft für Anlagen- und ReaktorSicherheit”
GTN model  Gurson–Tvergaard–Needleman Material Model
GSTP  General Support Technology Programme
HAADF  High-angle Annular Dark-field Imaging
Hap  Hydroxyapatite
h-BN  Hexagonal Boron Nitride
HEA  High Entropy Alloy
HEC  Hydroxyethylcellulose
HEMT  High-electron-mobility Transistor
HER  Hydrogen Evolving Half-cell Reaction
HLW  High-level Radioactive Waste
HMN  Hierarchical Modular Network
HP  Hot Pressing or Hydrothermal Process
HPGe  High-purity Germanium
HPLWR  High Performance Light Water Reactor
HREM  High-resolution Electron Microscopy
HRTEM  Resolution Cross-sectional Transmission Electron Microscopy
HZE  High (H) atomic number (Z) and energy (E)
IAEA  International Atomic Energy Agency
IBM  Ion-beam Mixing
IBMP  Institute for Biomedical Problems, Moscow
IEE  Institute of Electrical Engineering
ICP-MS  Inductively Coupled Plasma Mass Spectrometry
ICP-OES  Inductively Coupled Plasma Optical Emission Spectrometry
ILL  Institut Laue-Langevin
INFN  Italian Frascati National Laboratories
IOD  In-Orbit Demonstration
IPE  International Plant-Analytical Exchange
IPERION CH  EU Funded Project (Integrated Platform for the European Research Infrastructure ON Cultural Heritage)
IRIX  International Radiological Information Exchange
ISE  International Soil-Analytical Exchange
ISO  International Organization for Standardization
ISS  International Space Station
ITO  Indium Tin Oxide
ITRAP  H-2020 EU Project, Illicit Trafficking Radiation Assessment Program
KAERI  Korea Atomic Energy Research Institute
KARATE  Reactor Physical Program Code System
KARATE-1200  Reactor Physical Program Code System for VVER-1200 Reactors
KDE  Kernel Density Estimates
keff  Effective Multiplication Factor
KFKI  Former Name of the Research Centre, Nowadays the Campus Name
KIKO3DMG  Nodal Reactor Physics Calculation Code Developed in the CER
KIT  Karlsruhe Institute of Technology
L3PSA  Level 3 Probabilistic Safety Assessment
LC  Liquid Chromatography
LET  Linear Energy Transfer
LIBS  Laser Induced Breakdown Spectroscopy
LLNL  Lawrence Livermore National Laboratory
LOC  Lab-on-a-Chip
LOCA  Loss of Coolant Accident
LP  Linear Programming
LSC  Liquid Scintillation Counting
LTO  Long Term Operation
LWR  Light Water Reactor
MAT  Magnetic Adaptive Testing
MATTER  EU FP7 Project (MATerial TEsting and Rules)
MBA  Mercaptobenzoic Acid
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>MCNP</td>
<td>Monte Carlo N-Particle Transport Code</td>
</tr>
<tr>
<td>MELODI</td>
<td>EU Strategic Research Agenda for Low Dose Research</td>
</tr>
<tr>
<td>MEIS</td>
<td>Medium Energy Ion Scattering</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical System</td>
</tr>
<tr>
<td>MEPHI</td>
<td>Moscow Engineering Physics Institute</td>
</tr>
<tr>
<td>MFA</td>
<td>Institute of Technical Physics and Materials Science (Hungarian acronym)</td>
</tr>
<tr>
<td>MILC</td>
<td>Metal Induced Lateral Crystallization</td>
</tr>
<tr>
<td>MIS</td>
<td>Minimally Invasive Robotic Surgery</td>
</tr>
<tr>
<td>MLG</td>
<td>Multi-layered Graphene</td>
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<tr>
<td>MoM</td>
<td>Metal-on-Metal</td>
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<tr>
<td>MOS</td>
<td>Metal-oxide Semiconductor</td>
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<tr>
<td>MOX</td>
<td>Mixed Oxide</td>
</tr>
<tr>
<td>MPH</td>
<td>Material Property Handbook</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry or Mössbauer Spectroscopy</td>
</tr>
<tr>
<td>MTA EK</td>
<td>Hungarian Academy of Sciences Centre for Energy Research (Hungarian acronym)</td>
</tr>
<tr>
<td>MTBs</td>
<td>Mirror Twin Boundaries</td>
</tr>
<tr>
<td>MZI</td>
<td>Mach-Zender Interferometer</td>
</tr>
<tr>
<td>MU</td>
<td>Mock-up</td>
</tr>
<tr>
<td>MULTICELL</td>
<td>Reactor Physical Transport Code</td>
</tr>
<tr>
<td>MVM</td>
<td>Hungarian Power Companies</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multiwall Carbon Nanotube</td>
</tr>
<tr>
<td>NAA</td>
<td>Neutron Activation Analysis</td>
</tr>
<tr>
<td>NAL</td>
<td>Nuclear Analysis and Radiography Department, MTA EK</td>
</tr>
<tr>
<td>ND</td>
<td>Neutron Diffraction</td>
</tr>
<tr>
<td>NDE</td>
<td>Non Destructive Evaluation</td>
</tr>
<tr>
<td>NEAAA</td>
<td>Neutron-based Element Analysis and Activation Assessment</td>
</tr>
<tr>
<td>NEMS</td>
<td>Nano Electromechanical System</td>
</tr>
<tr>
<td>NII</td>
<td>Non-Intrusive Inspection</td>
</tr>
<tr>
<td>NIPS</td>
<td>Neutron Induced Prompt Gamma-ray Spectroscopy</td>
</tr>
<tr>
<td>NKFIH</td>
<td>National Research, Development and Research Office (Hungarian acronym)</td>
</tr>
<tr>
<td>NLD</td>
<td>Nuclear Level Density</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NMX</td>
<td>Neutron Macromolecular Diffraction</td>
</tr>
<tr>
<td>NKH</td>
<td>National Nuclear Research Program</td>
</tr>
<tr>
<td>NNK</td>
<td>National Nuclear Research Program</td>
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<tr>
<td>NOMAD</td>
<td>Non-destructive Evaluation System for the Inspection of Operation-Induced Material Degradation in Nuclear Power Plants (EU H2020 project)</td>
</tr>
<tr>
<td>NORM</td>
<td>Naturally-Occurring Radioactive Materials</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>NPP</td>
<td>Nuclear Power Plant</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>NR</td>
<td>Neutron Radiography</td>
</tr>
<tr>
<td>NRC</td>
<td>Nuclear Regulatory Commission</td>
</tr>
<tr>
<td>NUBIKI</td>
<td>Nuclear Safety Research Institute</td>
</tr>
<tr>
<td>OAH</td>
<td>Hungarian Atomic Energy Authority (Hungarian acronym)</td>
</tr>
<tr>
<td>OECD</td>
<td>Organisation for Economic Co-operation and Development</td>
</tr>
<tr>
<td>OECD NEA</td>
<td>Organisation for Economic Co-operation and Development, Nuclear Energy Agency</td>
</tr>
<tr>
<td>OKSER</td>
<td>National Environmental Radiation Protection Control System (Hung. Acronym)</td>
</tr>
<tr>
<td>ORC</td>
<td>Organic Rankine Cycle</td>
</tr>
<tr>
<td>OSJER</td>
<td>National Environmental Radiation Protection Control System (Hung. Acronym)</td>
</tr>
<tr>
<td>OTKA</td>
<td>Hungarian Scientific Research Fund (Hungarian Acronym)</td>
</tr>
<tr>
<td>OWLS</td>
<td>Optical Waveguide Light Mode Spectroscopy</td>
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</table>
Paks NPP  Paks Nuclear Power Plant
PBW  Proton Beam Writing
PCB  Printed Circuit Board
PCMI  Pellet-Cladding Mechanical Interaction
PCT  Peak Cladding Temperature
PDMS  Polydimethylsiloxane
PGAA  Prompt-gamma Neutron Activation Analysis
PGAI  Prompt-gamma Activation Imaging
PIE  Post Irradiation Examination
PIPS  Passivated Implanted Planar Silicon
PIXE  Particle-induced X-ray Emission or Proton-induced X-ray Emission
PL  Photoluminescence Spectrometer
PLL-g-PEG  Random Graft Co-polymer with a Poly(L-lysine) Backbone and Poly(ethylene glycol) Side-chains
POEA  Polyethoxylated Tallow Amine
PRD  Personal Radiation Dosimeter
PSA  Probabilistic Safety Analysis
PSI  Paul Scherrer Institute, Villigen, Schweiz
PSF  Photon Strength Function
PXRD  Powder X-ray Diffractometry
pXRF  Portable XRF Spectrometer
PWR  Pressurized Water Reactor
QCM  Quartz Crystal Microbalance
QMS  Quadrupole Mass Spectrometer
QRPA  Quasiparticle Random-phase Approximation
RAD  Static/dynamic Thermal-neutron and X-ray Imaging Station at BNC
RADCUBE  A Joint Mission Name of the ESA
RadMag  Instrument for Measuring Space Radiation and Magnetic Field Parameters
RBE  Relative Biological Effectiveness
RBS  Rutherford Backscattering
RF  Radio-frequency
RGD  Arg-Gly-Asp (peptide sequence)
RHA  Radiation Hardness Assurance
RHE  Reversible Hydrogen Electrode
RID  Radionuclide Identification Device
RMC method  Reverse Monte Carlo Method
RPM  Radiation Portal Monitor
RPV  Reactor Pressure Vessel
ROS  Reactive Oxygen Species
RRAM  Resistive Random Access Memory
RWG  Resonant Waveguide Grating
SAA  Sulphanilamide
SAED  Selected Area Electron Diffraction
SAFEST  EU Funded Project: Severe Accident Facilities for European Safety Targets
SANS  Small Angle Neutron Scattering
SBF  Simulated Body Fluid
SBO  Station Blackout
SBR  Signal-to-Background Ratio
SCC  Stress-Corrosion Cracking
SCWR  Supercritical Water Cooled Reactor
SEM  Scanning Electron Microscopy
SERS  Surface Enhanced Raman Spectroscopy
SGD  Sulfaguanidine
SI  Structural Integrity
SINE2020  EU Funded Project: Science and Innovation with Neutrons in Europe in 2020
SINAC  Simulator Software for Interactive modelling of environmental consequences of Nuclear ACcidents
SIS  Susceptible Infected Modular
SLM  Stochastic Lung Model
SMAD  Solvated Metal Atom Deposition
SMD  Solvation Model Density
SMX  Sulfamethoxazole
SNMS  Secondary Neutral Mass Spectrometry
SOC  Spin Orbit Coupling
SOD  Superoxide Dismutase
SOI  Si-on-Insulator
SOL  Sol Immobilisation Method
SP  Safeguards Support Programme
SPD  Severe Plastic Deformation
SPENVIS  Space Environment Information System
SPR  Surface Plasmon Resonance
SPS  Spark Plasma Sintering
SR  Synchrotron Radiation
SRA  Strategic Research Agenda
SRPM  Spectroscopic Radiation Portal Monitor
SS  Stainless Steel or Single Scattering
SSA  Space Situational Awareness
SSD  Solid-state Drive
SSNTD  Solid State Nuclear Track Detector
SWE  Space Weather Service Network
SZIKTI  Materials Research and Testing Laboratory for Silicate Industry Ltd., Budapest
SZTAKI  MTA Institute for Computer Science and Control
STEM  Scanning Transmission Electron Microscopy
STM  Scanning Tunnelling Microscopy
STZ  Sulfathiazole
SWV  Square Wave Voltammetry
TAV TPS HAS  Titanium-aluminium-vanadium/Plasma-sprayed titanium/Hydroxyapatite
TCD  Thermal Conductivity Detector
TEM  Transmission Electron Microscopy
TET  Bilateral Research Program (Hungarian acronym)
TFC  Trilateral Flash Cycle
TID  Total Ionizing Dose
TLD  Thermoluminescent Dosimeter
TMDC  Transition Metal Dichalcogenide
TNA  Technology Needs Assessment Project
TOAB  Tetraoctylammonium Bromide
TOF_surf  Turnover Frequencies Related to Surface
TOF-ND  Time of Flight Neutron Diffraction
TPD  Temperature Programmed Desorption
TPO  Temperature Programed Oxidation
TPR  Temperature Programmed Reduction
TRITEL  Three Dimensional Silicon Detector Telescope
TRL  Technology Readiness Level
TRT  Thermal Release Tape
T-VAC  Thermal-Vacuum Test
TXRF  Total-reflection X-ray Fluorescence
UFG  Ultrafine-grained
UOX  Uranium oxide
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTS</td>
<td>Ultimate Tensile Strength</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>Ultraviolet-Visible (Spectroscopy)</td>
</tr>
<tr>
<td>VERONA</td>
<td>Reactor Core Monitoring and the Reactivity Measurement System for VVER Type NPPs</td>
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<tr>
<td>VVER</td>
<td>Water-Cooled Water-Moderated Energetic Reactor, Russian acronym</td>
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<tr>
<td>VVER-SCP</td>
<td>VVER Supercritical Pressure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectrometry</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence Analysis</td>
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<td>YAG</td>
<td>Yttrium-aluminium-garnet</td>
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<td>YSZ</td>
<td>Yttria-stabilized Zirconia</td>
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<tr>
<td>WBC</td>
<td>Whole Body Counter or Tungsten Boron Carbide</td>
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<tr>
<td>WEPAL</td>
<td>Wageningen Evaluating Programs for Analytical Laboratories</td>
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<tr>
<td>WG</td>
<td>Work Group</td>
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<tr>
<td>WMDs</td>
<td>Weapons of Mass Destruction</td>
</tr>
<tr>
<td>zzMTBs</td>
<td>Zigzag Mirror Twin Boundaries</td>
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