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Book of abstracts

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2017 DIFFUSION FUNDAMENTALS

INTERNATIONAL CONFERENCE "Diffusion Fundamentals VII"

follows six biannual conferences in this series, held in

- **Dresden, Germany (2015)**
- **Leipzig, Germany (2013)**
- **Troy, NY, USA (2011)**
- **Athens, Greece (2009)**
- **L'Aquila, Italy (2007)**
- **Leipzig, Germany (2005)**

The **Diffusion Fundamentals Conferences** are held every two years. They represent a unique international forum bringing together the specialists from disciplines in different fields of materials science, chemistry, physics and engineering as well as archaeology, ecology, epidemics, ethnology, linguistics and sociology. They all are concerned with the phenomenon of random movement which is known to occur on molecular scales just as over macroscopic dimensions. Diffusion is thus among the major processes which decide over the final result of a large spectrum of phenomena. This made us suggest the question "**Evolution or Degradation?**" as one of the key topics of this year's "**Diffusion Fundamentals**" conference.

The abstracts in this book are divided in three chapters: invited, oral and posters. They follow in the alphabetic order of presenting authors.

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Invited talks

Diffusion NMR: From catalysts to gelatin, a useful tool for exploring structure and dynamics in porous networks

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Measurements and quantification of diffusion is crucial for understanding, designing and optimizing processes and product manufacturing. Several techniques have been developed over the years to quantify transport by diffusion in physical and chemical systems. Among the various methods, pulsed-field gradient (PFG) NMR is a very powerful tool for non-invasive measurements of diffusion coefficients, which can be applied to a wide variety of systems, some of which rather complex and inaccessible with other techniques. In this work several applications of the technique to systems of industrial relevance, including catalysts and gelatinous materials, will be presented. The technique can provide unique insights both on transport mechanisms and structural features of porous networks and how these features change during operation, which can be used for process and product design optimization.

Diffusive phase transformations in metallic glasses

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A large set of experimental results obtained by the author and colleagues related to the diffusion-related effects and phase transformation observed in metallic glasses will be presented and discussed. Structural changes observed in metallic glasses [1] on heating include structural relaxation (leading to densification and hardening of the glass) [2] and devitrification process which includes inverse glass-transition [3] to a supercooled liquid [4] and crystallization [5].

The step-scan mode specific heat capacity of the $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ and $Zr_{55}Cu_{30}Al_{10}Ni_5$ metallic glasses exhibited two different slopes within the glass-transition region related to the difference in diffusion coefficients of the alloying elements in these alloys [3].

Three types of diffusive phase transformations observed in the glassy alloys: polymorphous (a product phase has the same composition as the glassy phase), primary (a product phase has a composition different from that of the glassy phase) and eutectic (two or more phases nucleate and grow conjointly) [1] will be discussed. It will also be shown that in some glassy alloys phase separation by binodal or spinodal decomposition precedes crystallization [2].

Primary crystallization involving long-range diffusion and growth difficulties leads to the formation of nanoscale crystalline and quasicrystalline particles [5]. Formation of a nanostructure within the glassy phase leads to enhanced mechanical properties compared to fully glassy and crystalline alloys [2]. It will also be shown that $Fe_{48}Cr_{15}Mo_{14}C_{15}B_6RE_2$ (RE = Y or Tm) alloys are distinct from usual metallic glasses. Their glass-forming ability appears to be limited by the rate of crystal growth, and even rapidly quenched samples contain pre-existing nuclei of the χ-$Fe_{36}Cr_{12}Mo_{10}$ phase. This phase is formed because RE elements cannot be redistributed fast enough to trigger eutectic crystallization of the supercooled liquid. Calculations based on the diffusion coefficients indicate that slow diffusion of RE metals at the crystallization temperature does not allow solute partitioning to proceed to

completion and trigger eutectic crystallization observed in the RE metals free alloys. Because of these pre-existing nuclei, isothermal crystallization of the $Fe_{48}Cr_{15}Mo_{14}C_{15}B_6RE_2$ glasses occurs without an incubation period. The lack of incubation period, and the particles growth limitation rather than nucleation limitation, are in contrast to the behavior expected for bulk metallic glasses in general. Destabilization of the competing crystalline phases (to be formed by eutectic crystallization) is considered to be the dominant reason for the significantly improved glass-forming ability of these bulk metallic glassy alloys by RE metals. The low growth rate of the χ-$Fe_{36}Cr_{12}Mo_{10}$ phase, important for the GFA of $Fe_{48}Cr_{15}Mo_{14}C_{15}B_6RE_2$ is related to large, inhomogeneous internal strain in these particles. This strain, related to the large volume difference between the glassy and crystalline phases, is partly reduced but redistributed by the incorporation of slow-diffusing RE element in the crystalline phase.

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Multiscale Modeling of Water and Proton Diffusion in Self-Assembled Polymer Electrolyte Membranes

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Polyelectrolyte membranes composed of hydrophilic and hydrophobic fragments segregate upon solvation and form mesoscopic structures with interpenetrating hydrophilic and hydrophobic subphases. A typical example is Nafion polymer with sulfonate sidechains attached to perfluorinated backbone [1]. Water concentrates around the sulfonate groups in nanometer size clusters, which grow and coalesce into a 3-dimentional network of water channels as the degree of hydration increases. This segregated morphology determines the transport properties of Nafion membranes that are widely used as compartment separators in fuel cells and other electro-chemical devices, as well as permselective diffusion barriers in protective fabrics. We introduce a coarse-grained soft-core model of Nafion membrane, which accounts explicitly for polymer rigidity and electrostatic interactions, and is matched to atomistic molecular dynamics simulations. By means of dissipative particle dynamics (DPD) and Monte Carlo (MC) simulations, we explore geometrical, transport, and sorption properties of hydrated membranes of various composition. Molecular diffusion of water and proton in hydrophilic subphase of solvated membrane is studied with two methods: random walk in digitized 3D static replicas of the segregated membrane and in the course of dynamic DPD simulations. Novel methodology will be presented for coarse-grained modeling of proton transport accounting for vehicular and hopping mechanisms [2]. One of the interesting conclusions is the importance of the dynamics percolation effects related to the merge and rapture of water bridges between water clusters due to thermal fluctuations [3].

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Grain boundary junctions and grain growth in nanocrystalline materials

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The influence of grain boundary and interphase junctions on the thermodynamics and kinetics of grain growth in nanocrystalline materials is considered. The presented results of current experimental measurements of the grain boundary and grain boundary – free surface triple junctions give the opportunity to estimate quantitatively the influence of the junctions on the kinetics of the grain growth and on the evolution and stability of nanocrystalline systems.

Transport mechanisms in heterogeneous pore networks: from molecular to meso-scale observations

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Fluids under confinement exhibit interesting peculiarities and deviations from bulk behaviour. Understanding transport mechanisms and predicting transport properties is important for further developing applications such as catalysis and gas separation, and it is becoming essential for developing unconventional hydrocarbon reservoirs. Much can be learned from molecular simulations. We conducted equilibrium, and sometimes non-equilibrium molecular dynamics simulations for fluids, pure and mixed, confined within extremely narrow pores. We considered aqueous systems containing ethanol, H_2S, and methane, as well as organic systems containing alkanes of various molecular weights and CO_2. We will attempt to quantify and generalize the results, which suggest that depending on fluid composition, pore properties, and pore-fluid preferential interactions, a number of different mechanisms dictate the transport properties of the confined fluids. The results sometimes suggest radically different behaviour compared to bulk fluids, which is often the case when we analyse the solubility of gases (methane and H_2S) in confined water. While detailed experimental verification of the observations can be problematic, quasi-elastic neutron scattering (QENS) has proven useful. We will present recent attempts at reconciling observations form atomistic molecular dynamics simulations and QENS, which suggest that synergistic combinations of experiments and simulations yield a powerful tool to discover transport mechanisms in confinement. However, to further practical applications one needs to up-scale these insights. We will present a kinetic Monte Carlo approach, which yields insights useful in particular for quantifying the rate-limiting mechanisms that currently hinder the production of shale gas.

Oral talks

A Chapman-Kolmogorov approach for diffusion in an expanding medium

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A vast majority of studies devoted to diffusion assume that it takes place in a static medium. However, in a number of cases the medium growth or contraction takes place in time scales that are relevant for diffusive transport. For instance, in developmental biology, the formation of biological structures (e.g. the pigmentation of skin) occurs during tissue growth. Another example is the diffusion of cosmic rays in the expanding universe. Typically, two types of approaches are used to derive the relevant diffusion equation, namely a) a continuity equation based on mass conservation arguments and particle fluxes that depend linearly on concentrations b) a coarse-grained master equation formalism. Here, we present an alternative approach based on a random walk model that naturally leads to a Chapman-Kolmogorov equation [1]. For the case of a 1D power-law expansion, we find striking crossover effects depending on the exponent γ characterizing the medium growth. The mean square displacement grows linearly in time when $\gamma<1/2$, but is proportional to $t^{2\gamma}$ when $\gamma>1/2$. In the marginal case $\gamma=1/2$ there is a logarithmic correction to the linear increase in time. Beyond this, there are further consequences at the level of propagator. When $\gamma>1/2$, particles are not able to efficiently spread across the whole medium, and this leads to strong localization effects and poor mixing of two diffusive pulses that have a minimum initial separation (see Fig. 1). In this case, a strong memory of the initial condition persists in the long time regime. Finally, the probability for a diffusive walker starting from the center of a growing sphere to cross its surface becomes less than one when $\gamma>1/2$. When $\gamma=1/2$, the n-th order moment of the first passage time may or may not exist depending on whether the diffusivity D exceeds an n-dependent threshold value. We discuss possible implications of our findings for a number of real systems as well as some preliminary results for anomalous diffusion processes.

Atomistic interpretation of the interface transfer coefficients for interdiffusion in AB binary phase separating system

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During intermixing in *A/B* diffusion couple the actual compositions (c'_α and c'_β) on the left as well as on the right hand side of the α/β interface gradually will decrease (from unity) as well as increase (from 0) until the equilibrium c_α and c_β will be reached (α and β refer to the A- and B-rich phases, separated by the interface). The diffusion flux of A atoms across this interface, J_I, is determined from the expression of atomic fluxes given in the modified Martin model [1,2]. Assuming that J_I, is proportional to the deviations, $\Delta_\alpha=c'_\alpha - c_\alpha$ and $\Delta_\beta=c_\beta - c'_\beta$, from the equilibrium

$$J_I=(1/\Omega)[K_{I\alpha\beta}\Delta_\alpha + K_{I\beta\alpha}\Delta_\beta),$$

where $\Omega=\Omega_A=\Omega_B$ is the atomic volume. It is shown that the $K_{I\alpha\beta}$ and $K_{I\beta\alpha}$ interface transfer coefficients are positive and equal to each other for symmetric miscibility gap and can be given as

$$K_{I\beta\alpha}= K_{I\alpha\beta}=K= z_v a\Gamma_{I\alpha\beta}c_\alpha\xi.$$

Here $\Gamma_{I\alpha\beta}$ is the jump frequency from α to β phase across the interface, a is the lattice parameter z_v is the vertical coordination number, $\xi=[1+\exp(ZV\{c_\alpha-c_\beta\}/kT)]$, V is the well-known solid solution parameter, kT has its usual meaning. The above expression justifies the conjecture, frequently used in the literature (see e.g. [3]), that *only one interface transfer coefficient is enough for the description of mass transfer across an interface*. For short diffusion times the finite value of $\Gamma_{I\alpha\beta}$ will restrict the flux, leading to linear kinetics. It will also be shown that for the estimation of the critical interface shift (giving the transition from the interface to diffusion control, i.e. from linear to parabolic kinetics) the

$$x_c\cong a\exp[-ZM(1-2c_\beta)/kT]$$

relation can be used, where a is the lattice spacing and the exponential factor is the ratio of factors describing the composition dependence of the jump frequencies in the β phase and across the interface, respectively. Thus x_c is independent of the value of V and only the composition dependence of the jump frequencies is important. For composition independent jump frequencies $x_c \cong a$, (i.e. it can not be detected), while for the case when the diffusivity changes by seven orders of magnitude from pure A to B [2,4], x_c is about 150nm.

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Atomic interaction in grain boundaries and related phenomena

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Atomic segregation at grain boundaries (GB), as a result of atoms interaction with GBs, has a prolonged history [1]. The fact that grain boundary diffusion (GBD) is moderated under the action of grain boundary segregation (GBS) is now generally recognized.

Meanwhile, at the case of heterodiffusion, except of atoms interaction with GB, it is necessary to take into account atoms interaction between them in GB. Such interaction leads to the formation of atomic complexes. This conclusion is based on the results of thermodynamic study [2,3] and results of computer simulation which showed the possibility of B2 type complexes formation in Fe-Al system, a deviation of solute-solute coordination number from random distribution [4] and decrease of mean square atomic displacements (MSD) [5]. The last effect can be possibly connected with recently observed absence of the accelerated GBD Fe and Co in Cu compared with bulk diffusion [6,7].

At the present talk the peculiarities were studied of grain boundary self diffusion in Cu connected with the effect of atomic pairs formation in GBs.

The molecular dynamics (MD) simulation of GB selfdiffusion was used taking semiempirical potential designed for Cu [8,9]. To be sure in adequacy of the model proposed, the double product (δD_{gb}, where δ is a width of GB and D_{gb} is a coefficient of GB selfdiffusion) of GB selfdiffusion was obtained based on MSD of free atoms at different temperatures (825, 900, 1000 and 1200K).

The results obtained for δD_{gb} and D_{gb} (δ is taken as 0,5 nm) are in a good agreement with experimental results [10,11] and other results of computer simulation [12] taking into account a difference in chosen potentials and types of GBs.

The results are compared with similar simulation but with artificial addition the energy of interaction (E) between identical atoms in arbitrary chosen pairs. To obtain reliable data on the MSD at comparatively low temperatures the used simulation cell consists of three thousands atoms, two symmetrical GBs Σ5 (001)(012) and 70 pairs of identical random Cu atoms in GBs

bonded into pairs. It was required also that MD should run at least 100ps.

It was shown that the complexes formation leads to decrease of MSD for atoms bonded into the pair compared with free atoms. The pair interaction energy E=-0,2 eV/atom influences only slightly on D_{gb} which decreases to 15-45% comparing with E=0. The activation energy changes in limits of error. At E=-0,5 eV/atom Dgb decreases more than at order of magnitude and activation energy increases at 1,5 times comparing with E=0.

The results obtained involve also dependence the number of the stable pairs on time and temperature and show the possibility of pairs to condense into ternary, quarterly and more numerous complexes.

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Effects of surface modifications on molecular diffusion in mesoporous catalytic materials

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In this work, we use pulsed-field gradient (PFG) NMR to probe molecular diffusion of liquids inside mesoporous structures and assess the influence of surface modifications, namely, deposition of palladium (Pd) nanoparticles over alumina (Al_2O_3) surfaces and passivation of titania (TiO_2) surfaces with alkyl chains, on the diffusion pattern.

Diffusion of binary mixtures acetone/chloroform inside Al_2O_3 and Pd/Al_2O_3 is investigated. The deposition of Pd nanoparticles onto the Al_2O_3 surface leads to a reduction of the diffusion coefficient of guest molecules inside the pore network, suggesting that Pd particles obstruct some diffusion pathways, hence, increasing the average tortuosity of the pore network.

The effect of surface passivation, by replacing –OH surface groups of TiO_2 with octyl aliphatic chains, is also assessed by using primary alcohols, in the range C_1-C_8. The experiments show that in the bare TiO_2 sample, higher alcohols show a behavior of enhanced diffusion, relative to the diffusion expected based on tortuosity values, which is attributed to a hydrogen bonding network disruption, which has been previously observed when studying diffusion of alcohols and polyols in mesoporous materials.[1,2] Removal and replacement of –OH surface groups in bare TiO_2 by octyl chains leads to a diffusion behavior inside the pore space that is independent of alcohol chain length. In particular, the apparent tortuosity of all the C_1-C_8 alcohols becomes the same and equal to that measured using weakly-interacting molecules such as alkanes, the latter being considered the true estimate of the tortuosity of the pore structure. This shows that the presence of –OH groups over the surface, and hence the chemistry of the surface, is an important factor in affecting diffusion of alcohols inside the pore space.

In summary, the work shows that changes in surface properties change diffusion mass transport in pore networks, which may be a factor to consider when using such materials in catalytic applications.

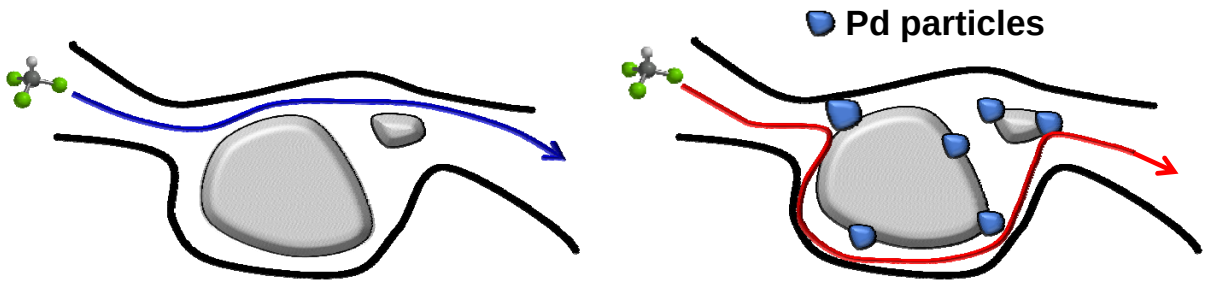

Figure 1: Schematic of diffusion path in **(left)** Al_2O_3 and **(right)** Pd/Al_2O_3 of a chloroform molecule. Pd particle deposition might influence the diffusion path and hence the tortuosity of the structure.

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Phase stability and stress evolution of nano-multilayered coatings upon thermal treatment

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The functionality, reliability and service lifetime of nano-multilayered (NML) devices and components are largely affected by the stress evolution during fabrication, processing and operation. Hence a comprehensive experimental assessment of their structural integrity, including stress state evolution, during thermal loading is a crucial step to evaluate their applicability. This contribution addresses recent advances in the experimental investigation of the phase stability, microstructural integrity and stress evolution of metal/metal (Cu/W) [1] and metal/ceramic (Ag/AlN, Ag60wt.%Cu40at.%/AlN, AgGe10at% /AlN) NML coatings during heating by advanced in-situ diffraction methods in combination with XPS, SEM and TEM analysis: see Fig.1. Such NML systems, as prepared by conventional magnetron sputtering, are envisaged as novel nano-structured brazing filler materials for advanced joining applications [2]..

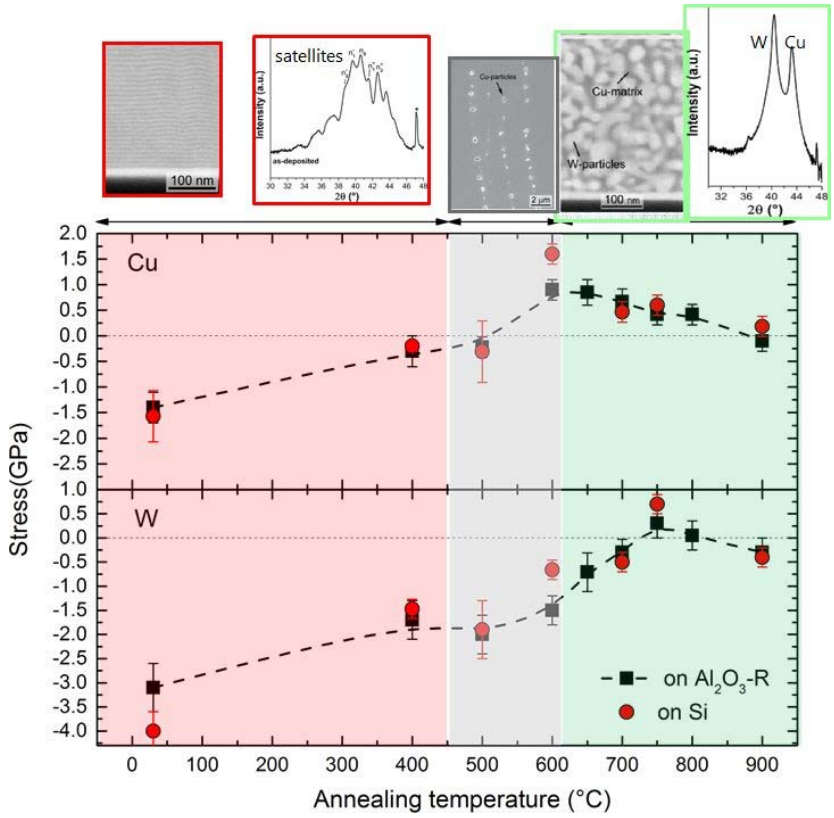

Figure 2: Stress evolution of Cu, W layers combined with SEM morphologic analysis

It is shown that the Cu/W NMLs gradually transform from a nano-laminated into a nano-composite structure upon heating at T >750°C, as accompanied by a complete relaxation of the compressive growth stresses in the confined Cu and W nanolayers. On the contrary, fast heating of the Ag/AlN NMLs in air invokes massive mass transport of Ag from the NML interior to the coating surface at temperatures as low as 200°C (i.e. much below the Ag bulk melting point), as accompanied by a fast relaxation of thermally-induced compressive stresses [3]. The crucial role of the processing atmosphere and of co-alloying elements like Cu and Ge on the phase stability and compressive/tensile stress determination of the Ag-based NMLs is rationalized.

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Curvature effects on a phenomenological reaction-diffusion model of biodegradation

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The biodegradation process of some types of polymers occurs due to many different factors including their morphology, structure and chemical composition, etc. Although this is a complicated process, most of its important stages like the diffusion of monomers and the hydrolysis reactions have been modeled phenomenologically through reaction-diffusion equations, where the properties of the polymers were encompassed [1].

Using a reaction-diffusion model for the biodegradation of polymers [1], we study in this contribution the possible effects of the curvature of the system geometry in the degradation process, which is characterized by the interaction of the corresponding reaction rate and the diffusion coefficient.

It has been shown that the curvature of the system plays an important role in confined diffusion processes [2, 3] and instability criteria in pattern formation in reaction-diffusion systems [4, 5]. In particular the solution region changes due to the particular geometry of the problem.

To illustrate the problem of diffusion on a curved surface, we consider the so-called Gaussian bump [6]. We choose this surface because mathematically, its metric depends only on one variable so its analysis can be simplified. Physically contains positive and negative curvatures about its waist, and zero in the asymptotic limit.

We show how the curvature differences influences the relation between diffusion and reaction rate that moderates degradation.

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Theory of nonequilibrium grain boundaries and its applications to describe ultrafine-grained metals and alloys produced by ECAP

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The research presents key approaches to describing the features of evolution of structure and physical and mechanical properties of ultrafine-grained (UFG) metals and alloys obtained through equal channel angular pressing (ECAP).

It was shown that the specificity of UFG materials from the defect theory perspective lies in the fact that most processes controlling their behavior and properties develop not in the crystal lattice (grains) like in conventional materials but rather in grain boundaries. The main type of defects in UFG materials defining the nature of these processes are neither dislocations nor vacancies (as in conventional materials) but rather inner interfaces. The key features of grain boundary processes are determined by the interaction of grain boundaries with dislocations and point defects getting in there from the lattice.

To describe structural features and properties of UFG materials, a theory of nonequilibrium grain boundaries in metals and alloys was proposed [1, 2].

It was shown that the structure of grain boundaries could be described using the so-called 'island model'. The key parameter that characterizes the structural condition of grain boundaries is free volume. It was shown that anomalies in diffusion parameters and thermodynamic characteristics of nonequilibrium grain boundaries arise from the increase in their free volume driven by the free volume introduced by lattice dislocations that get into the grain boundaries. Expressions were obtained that describe changes in the energy of grain boundaries and their diffusion parameters during their interaction with individual dislocations and lattice dislocation flows. The dependence is determined between the grain boundary diffusion ratio and deformation rate, as well as the material structure parameters.

Based on the theory of nonequilibrium grain boundaries, processes controlled by diffusion in nonequilibrium grain boundaries were reviewed. Descriptions were provided as to the features of grain boundary diffusion, grain boundary sliding, recovery and recrystallization processes, superplasticity, features characterizing the evolution of mechanical properties in materials with nonequilibrium grain boundaries such as UFG metals and alloys obtained through ECAP.

The report pays special attention to the issue of thermal stability of mechanical properties of UFG metals and alloys. The results of experimental and theoretical studies into return and recrystallization processes during annealing of UFG metals and alloys were described.

It was shown that the structural condition of grain boundaries is one of the key factors affecting the mechanical properties of UFG metals: during ECAP, UFG materials form grain boudaries that contain enhanced density of introduced defects which create long-range inner stress fileds. This leads to anomalies in mechanical properties of UFG materials at room temperature (deviation from the Hall-Petch relation, the effect of simultaneous increase in strength and ductility, the effect of optimal grain size for superplasticity, etc.).

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Adsorption and Diffusion Phenomena in Crystal Size Engineered ZIF-8 MOF

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ZIF-8 is a flexible zeolitic imidazolate framework (ZIF), member of the metal–organic framework (MOF) porous materials, whose narrow pore structure swings open by reorientation of imidazolate linkers and expands at high loading of guest molecules. This nanoporous material has been identified as a potential candidate for the energy-efficient adsorptive recovery of alcohols from diluted aqueous mixtures, such as obtained with the acetone-butanol-ethanol (ABE) fermentation [1].

In this work, the crystal size dependency of both structural transitions induced by N2 and Ar adsorption was investigated, from which the results, obtained with a volumetric technique, will be presented. On the other hand, the diffusion of n-butanol into well-engineered ZIF-8 crystals with identical surface area and micropore volume was also explored. Results acquired with two gravimetric methods (static and dynamic versions) will be shown. It was found that the crystal downsizing of nanoporous ZIF-8 adsorbent affects its structural flexibility observed from the equilibrium adsorption and desorption data of N2 and Ar. Adsorption kinetics of n-butanol in ZIF-8 showed to be strongly influenced by the crystal size, however, not according to a classical intracrystalline diffusion mechanism. Our results suggest that the structural transitions and uptake rates are dominated by crystal surface effects. Crystal downsizing increases the importance of such surface barriers [2].

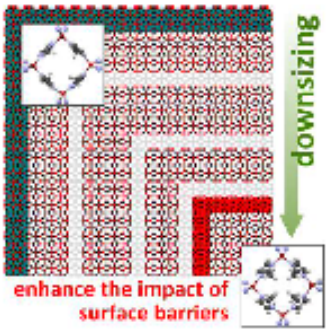

Figure 1: Schematic representation of the effect of crystal-downsizing on the enhancement of the contribution of surface barriers in the structural transition and uptake of guest-molecules by a nanoporous ZIF-8 crystal [2].

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Kirkendall effect on the nanoscale

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Kirkendall shift has been studied experimentally as well as theoretically for decades already. There are theoretical indications, that the Kirkendall effect must operate from the beginning of the diffusion process but there are practically no measurements on this short time and lenght scale. For that reason, diffusion on the nanometer scale was investigated experimentally the in different binary systems in thin film geometry. We followed the diffusion process as well as the Kirkendall effect by different methodes (TEM, SNMS and synchrotron X-ray waveguide technique). Investigations were performed in systems with complete soubility (BiSb, CuNi, BiSb) as well as in systems forming intermetallic phase (FeSb, FePd). It was found that with these methodes the Kirkendall shift can be well followed on the nano-scale. In FeSb system even the bifurcation of the Kirkendall plane was observed.

Phase separation in binary alloys under temperature / pressure action: valence electron energy as origin

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Formation and stability phases in binary alloys are defined by several factors as atomic size differences, electronegativities and Hume-Rothery effects. The classical example of the Hume-Rothery phases is the Cu – Zn diagram and related diagrams where the phase boundary restricted by the number of valence electrons per atoms or electron concentration. The physical basis was given within the model of the Fermi sphere – Brillouin zone (FS-BZ) configuration assuming the gain in the band structure energy by the contact of the Fermi sphere to the Brillouin plains and formation of the energy gaps (see [1, 2] and refs. therein). The FS-BZ approach can be extended for understanding of great variety of phase transitions in binary alloy systems under temperature or pressure action.

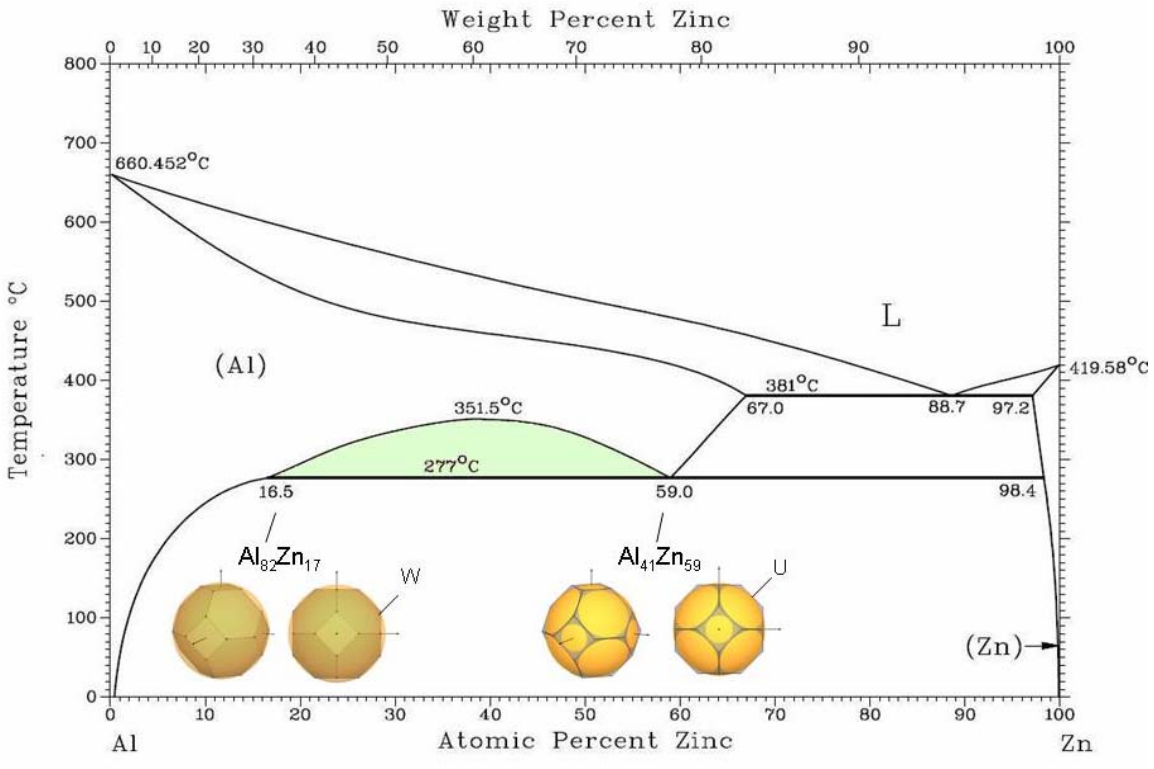

Figure 3: The phase diagram Al – Zn. The Al(Zn) solid solution region with the *fcc* structure contains a miscibility gap with two-phase region (colored). For the boundary phases with ~17 and 59 at% Zn constructions

of FS-BZ are given with a common view and a view along a*.

For polyvalent metals the volume of the valence electrons in the FS is large than the volume of the BZ. Therefore the Fermi surface cuts many zone planes and contributions to the crystal energy from regions near the plane intersections may lead to important effects for phase stability. An interesting case of the *fcc* phase decomposition is observed in the Al – Zn alloy system, where Al(Zn) *fcc* solid solution is stable at high temperature and below 352^{o}C there is a miscibility gap of two *fcc* phases with ~17 and 59 at.% Zn. The contacts FS with BZ occur for W-type corners and for the edges of (111) planes in the point U, respectively (Figure 1). In this case the electronic structure factor reveals as driving force for diffusion and phase separation.

Phase separation under pressure was observed for binary compound In_5Bi_3 at 15 GPa and 150^{o}C [3]. Two phases of different compositions were found with tetragonal distortions of the body-centered cubic phase with axial ratios c/a > 1 and c/a < 1. There is an example of chemically ordered compound decomposition with diffusion into two disordered phases. Structures of high-pressure phases follow the Bain path of tetragonal distortion and defined by minimization of the valence electron energy [3].

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Atomic Density Function approach to model the carbon kinetics in martensite

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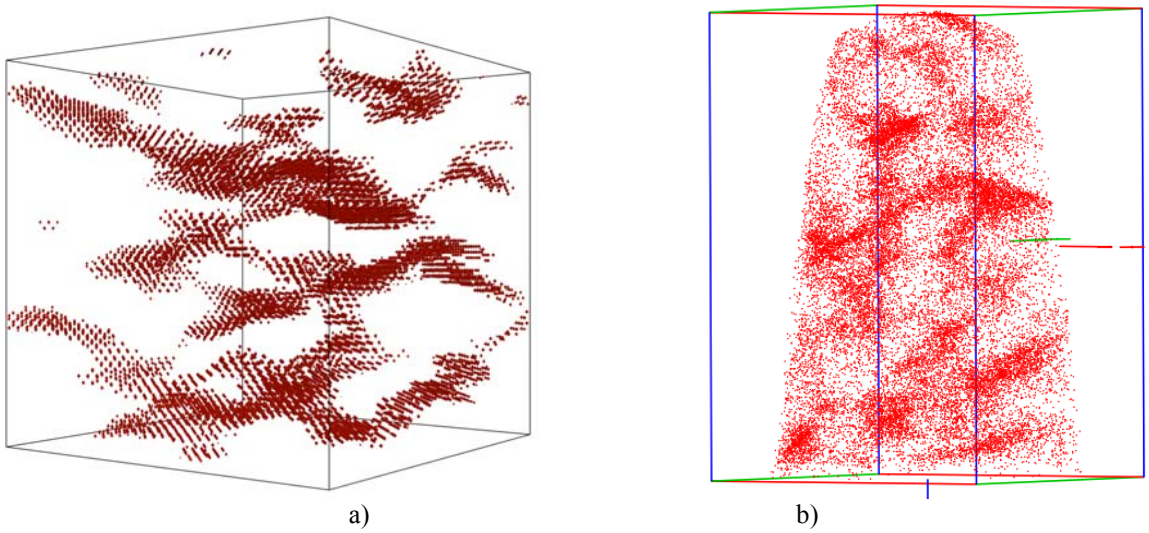
Carbon steels is the structural material by far the most used by man, and its importance in the global economy is paramount. This steel is Fe-C interstitial solid solution based on the low temperature bcc host lattice (α phase) and high temperature fcc solid solution (γ phase). Among its various forms, martensite obtained by rapid quenching the fcc austenite is the one with the highest strength. However, iron carbon martensite is not stable at room temperature and forms compositional modulations of carbon atoms during aging. It was shown experimentally that at the beginning these nanometric carbon-rich zones have Fe_8C composition and then undergoes C atom ordering within octahedral sublattices of the host Fe lattice. These carbon rich zones change drastically the mechanical properties of martensite. Consequently, it's extremely important to understand the phenomena related to low temperature (T<150°C) aging of the martensite in order to assist any further development of high strength steel.



a) b)

Figure 4: Redistribution of carbon atoms in the martensite aged 7 days at room temperature a) simulation results and b) 3D atom probe images. The carbon atoms are indicated in red.

In this study the Atomic Density Function (ADF) theory [1-4] has been applied to model the low temperature kinetics of carbon redistribution in martensite phase. It was shown that at early stage of aging the carbon kinetics is governed by the spinodal decomposition and small carbon rich zones appear. Then during further growth these zones are elongated to some special crystallographic directions to minimize the elastic energy of system. The simulated and experimental images of carbon redistribution in tempering martensite are shown in Figure 1. It should be noted that simulation results are in very good agreement with experimental data obtained by Atom Probe Tomography (APT).

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Influence of heat treatment on magnetic properties of Cu-Sn-Co-based materials produced by powder metallurgy

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In the foundation of this work is the issue for production of non-magnetic materials with predetermined weak magnetic properties. Preferable solution is to dope these materials with ferromagnetic impurities in low concentrations. One of the efficient ways to obtain such materials is the use of powder metallurgy which gives an opportunity to produce complex powder compositions with variety of components in precisely specified concentrations.

As an research object powder compositions of systems Cu-Sn (8 wt. % Sn) and Cu-Sn-P (8 wt. % Sn; 0,5 wt. % P) with the addition of 1,5 wt. % Co were chosen. After mixing and pressing all samples were heat treated at 800 ˚C with different cooling rates.

Noticeable solubility of components in Cu-Co system is observed at high temperatures [1]. This fact makes it possible to form specified magnetic properties only by formation of metastable solid solution with the further annealing in order to exclude Co particles from Cu (reduce Cu concentration in Co solid solution) and change the quantity of ferromagnetic domains in material [2]. Experimental results in this work with fast cooled Cu-Sn-Co system samples showed the same except there was no solubility of Co in Cu-Sn matrix. Anyway Co-Cu solid solution formation reduces sample magnetization in comparison with the pressed one. Formation of Cu-Sn-Co solid solution was discovered only after Cu_3Sn chemical compound started to grow due to lower cooling rates. In the second case saturation magnetization became lower than for fast cooled sample because diffusion of Co into Cu-Sn solid solution was appeared and consequently the amount of ferromagnetic Co decreased.

In the fast cooled samples of Cu-Sn-P-Co system besides the partially dissolution of Cu in Co diffusion of phosphorus in Cu-Sn matrix with further formation of Co_2P chemical compound was occurred. Presence of cobalt phosphide decreased magnetic properties drastically because of paramagnetism of Co_2P [3]. In slow cooled samples additional phase of eutectic copper phosphide Cu_3P was discovered and saturation magnetization rose. Investigation of samples with various cooling rates proved that with the formation of tin-rich phase caused the dissolution of Co_2P with simultaneous diffusion of phosphorus to the boundaries of Cu_3Sn phase and formation of Cu_3P.

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Size dependent spinodal decomposition in Cu-Ag nanoparticles

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Nanoparticles are of considerable interest, owing to their size-dependent properties, different from those of bulk materials. For revealing internal atomic processes in them, individual nanoparticles of Cu-Ag alloys were grown by direct current (DC) magnetron sputtering. Phase-separation during growth in Cu-Ag particles was found to be size- and composition-dependent. Particles below 5 nm in diameter grow as a solid solution of the components for all compositions (15–80 at% Ag). In the low Ag content range (15 and 30 at% Ag) phase-separation occurs only for particles above 5 nm in diameter. The separation into Cu-rich and Ag-rich domains, when observed, takes place by spinodal decomposition for all particle sizes. In particles undergoing incomplete coalescence, phase-separation occurs even if the diameter of the colliding particles is below 5 nm. In the higher Ag content range (60-80 at%), however, no phase-separation is observed until coalescence sets in. Lattice parameter measurements in alloy particles of 30 at% Ag revealed that the miscibility gap in individual particles varies between 70 and 90 at%. Calculation of the composition dependence of the critical length for spinodal decomposition based on the Cahn-Hilliard theory provided quantitative explanation for the observed phenomena. [1] Besides, computer simulations using the Stochastic Kinetic Mean Filed model (skmf.eu, open source) [2] have also been performed which confirmed the results of the analytical calculations.

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Experimental evidences for anomalous grain boundary diffusion of Fe in Cu and Cu-Fe alloys

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Grain boundary diffusion in the Cu-Fe system is still an issue despite a well-developed methodology of grain boundary diffusion measurements. Rare results obtained for this system by different authors have been published so far [1-4] and they are contradictory to some extent.

The aim of the present study is to complete the published previously measurements and to clarify the specific behaviour of Fe in Cu. Fe grain boundary diffusion is studied in 99.995 wt.% pure Cu and the Cu-Fe alloys with iron contents of 0.18, 0.45, 0.6 and 0.8 wt. % using the radiotracer technique. A series of isothermal experiments at 1000 K reveals that the triple product of iron grain boundary diffusion is almost independent on the iron content excepting the alloy containing 0.8 wt. % of Fe where the triple product is increased by three orders of magnitude. Additional experiments at 1100, 900 and 717 K using this alloy confirm the anomaly observed at 1000 K, namely the triple product is continuously increasing following the Arrhenius dependence from 717 K to 1100 K except the temperature of 1000 K, where the triple product is anomalously high.

The obtained results are analyzed applying thermodynamic calculations of Fe and S solubility in Cu. It is suggested that the observed anomalies are related to a change of the grain boundary structure associated with a phase transition occurring in the Cu-Fe alloys.

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Recent advances in the study of high molecular mass polymer melts diffusion by proton NMR

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In high molecular mass polymer melts due to the linear structure of macromolecules and their mutual uncrossability a region of anomalous diffusion cover a very broad space/time interval. It extends up to the terminal relaxation time of a macromolecule $\tau_1 \propto \tau_s N^{3,4}$, where τ_s is the segmental relaxation time and N is a number of Kuhn segments per chain. During the time τ_1 polymer segments are displaced due to the thermal motions on a length scale on the order of a polymer chain linear size $R_F = bN^{1/2}$, where b is the Kuhn segment length. Proton spin relaxation, i.e. longitudinal (spin-lattice) and transverse (spin-spin) relaxation, is mainly determined by the magnetic dipole-dipole interactions between different protons, which can be both intermolecular and intramolecular. During many decades it was assumed analogously to the solid state NMR that proton spin relaxation in polymer melts is mainly determined by an interaction between the nearest protons from the same macromolecule, and magnetic dipole-dipole intermolecular contribution to different NMR phenomena connected with spin relaxation were completely ignored. Recent progress in theory and experiments devoted to the proton spin relaxation in polymer melts shows that due to the strongly anomalous nature of polymer segments diffusion on a very long time scale, $t \le \tau_1$, relative contributions from the intermolecular magnetic dipole-dipole interactions in NMR phenomena like spin-lattice relaxation, different types of proton spin echoes, double quantum resonance etc. are essentially different. The mentioned contributions are directly connected with the relative mean-squared displacement of polymer segments from different polymer chains, which opens new possibilities for experimental

investigations of anomalous diffusion in polymer melts on the length-scale of $10-200\,\text{Å}$, corresponding at temperatures high enough above the glass transition temperature to times on the order of $10^{-9}-10^{-2}\,s$.

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The Secret of the Maya Blue: A problem of diffusion in a microporous solid

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The adsorbed ^{129}Xenon detected by NMR is an excellent probe to determine microporous solid properties difficult to detect by classical physico-chemical techniques [1,2]. Indeed the very large and extremely polarisable electron cloud of xenon makes this atom particularly sensitive to its immediate environment. Small variations in the physical interactions with the latter cause marked perturbations of the electron cloud which are transmitted directly to the xenon nucleus and greatly affect the NMR spectrum. The corresponding chemical shift depends on the dimensions and structure of the free space, on the chemical composition of the pore walls and on the ease of diffusion of the atoms in the crystallites. This technique has been mainly used to solve the secret of the Maya Blue (MB) synthesis which is also a problem of diffusion in micropores [3].

The famous pre-Columbian Maya Blue pigment (2600 years b.c.) has been the subject of much research aimed at explaining the extreme stability of this hybrid organic/inorganic pigment present in mural paintings in Mayan Temples in the Yucatan, in many ceramic objects, in the large monolith, *Tlaltecuhtli,* representing the Aztec Earth god, etc.

In the MB pigment, the host is palygorskite clay (with tunnels having a 3.7 x 6.4 Å cross-section for the hydrated form), and the guest is the indigo molecule ($C_6H_{10}N_2O_2$). Depending on the various authors, the indigo lies in grooves at the surface of the clay fibers, inside the tunnels where it replaces the zeolitic water, or stays at the tunnel entrances. For this reason this research is focused on the mechanism of MB preparation and the final location of the indigo.

The dye was added to clay in three ways: i) the traditional Mayan technique, where palygorskite is mixed with an aqueous extract of leaves of the añil plant; ii) the synthetic method where the clay is mixed with synthetic indigo, either finely ground and heated to 180 °C or dissolved

in DMSO, since it is not soluble in water. The treatment in an Accelerated Weathering Tester to simulate ageing corresponds to 10 years in real time.

NMR spectra of ^{29}Si, ^{27}Al, ^{13}C and mainly adsorbed xenon ^{129}Xe show that, after ageing, only the sample prepared by the traditional technique contains indigo inside the palygorskite tunnels. With samples prepared from synthetic indigo, an interaction between indigo and the external surface of the clay is favoured.

Acid treatment of samples after ageing provides evidence for the chemical resistance of pigments prepared by the traditional technique as compared to the synthetic samples. This result agrees with the distribution of dye in the samples, as elucidated by NMR.

The indigo dye from añil leaves is water-insoluble; therefore, it must be deposited on the wall of the vessel and on the external surface of the clay without diffusion into the pores, according to the results on the synthetic samples. NMR spectra prove that indoxyl, a smaller precursor of indigo from añil leaves, is adsorbed on the clay surface and diffuse more easily into the pores, where it is ultimately oxidized by atmospheric oxygen, UV and hot climate, to provide indigo.

These results have resolved the mystery regarding the preparation of MB and its final state.

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Dynamic Light Scattering (DLS) for the characterization of diffusion processes

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Dynamic light scattering (DLS) represents a non-invasive technique to study diffusion processes in fluids. It is based on the analysis of microscopic fluctuations originating from the random thermal movement of molecules in macroscopic thermodynamic equilibrium. At present, the most frequent application of DLS is the study of collective diffusion coefficients for the characterization of macromolecular or particle size and size distribution. In this regard, the application of DLS from bulk fluids can be found nowadays, for example, for aerosols, colloidal dispersions, polymer solutions, solutions and dispersions of biological macromolecules and systems including viruses, protein-complexes, and membrane vesicles as well as for glasses, gels, and liquid crystals. In contrast to the application of DLS to study the dynamics and structure of diverse systems, there are currently only few research groups which use DLS to a greater or lesser extent for the determination of thermophysical properties. Here, a fundamental advantage is given by the fact that DLS may be used in thermodynamic equilibrium.

The present contribution summarizes and reviews the activities performed at the Department of Chemical and Biological Engineering (CBI) and the Erlangen Graduate School in Advanced Optical Technologies (SAOT) of the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU) as well as by different research groups worldwide during the past five decades in the field of thermophysical property research and in particular of diffusion measurements in fluids by DLS. The continuous progress in this field is given in retrospect, covering the first steps since helium lasers became available in the 1960s until today. The representation of the methodological principles of DLS and its experimental realization includes light scattering from bulk of fluids on a molecular level as

well as from particles and macromolecules in solution or, in general, from heterogeneous systems. Measurement examples are presented for the variety of thermophysical properties accessible by DLS from the bulk of fluids focusing on mass and thermal diffusivities. Here, limitations of the method regarding the thermodynamic state and the accuracy will also be discussed in detail. Finally, examples for mass and thermal diffusivities for specific working fluids in chemical and energy engineering obtained by DLS at CBI and SAOT Erlangen are given. The objects of investigation cover refrigerants, organic Rankine cycle (ORC) fluids, biofuels, liquid organic hydrogen carriers (LOHCs), ionic liquids (ILs), and Fischer-Tropsch systems. Current research activities contribute significantly to a reliable database for different working fluids, see, e.g., Refs. [1-3], and provide also answers to fundamental questions regarding the theory behind the method with respect to multi-component mixtures [4].

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MASS DIFFUSIVITIES OF BINARY MIXTURES OF NORMAL ALKANES WITH DISSOLVED GASES

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Knowledge on the mutual diffusivities of gases dissolved in liquids is of increasing interest for the optimization of processes such as the Fischer-Tropsch synthesis of high valued petroleum products from synthesis gas or the separation of flue gas components. Here, mass transfer is often the rate limiting step compared to, e.g., chemical reactions and/or heat transfer. In a related research project, the benefits of experimental and modelling methods are combined to get a better understanding on how molecular diffusion is affected by the characteristics of the mixture components, which contributes to the development of reliable predictions.

In the present contribution, dynamic light scattering (DLS) experiments and molecular dynamics (MD) simulations were performed at macroscopic thermodynamic equilibrium for a first set of model systems based on liquid normal alkanes and dissolved gases. The solvents *n*-hexane and *n*-decane in their binary mixtures with the solutes hydrogen, helium, nitrogen, and carbon monoxide were studied over a broad temperature range from (298 to 423) K at gas mole fractions below 5%. With DLS, the relaxation behavior of microscopic fluctuations in the properties of state is analyzed. In the case of concentration fluctuations in binary mixtures, their mean decay time is related to the mutual diffusivity which can be accessed by DLS in an absolute way without calibration. The present measurements document that even for small gas concentrations implying weak light scattering signals, reliable mutual diffusivities with typical uncertainties below 5% ($k = 2$) can be obtained. These results serve as a database for MD simulations. Here, thermophysical properties are computed by investigating the dynamics of molecules interacting with each other. Based on suitable models for the mixture components, the self-diffusion coefficient of the gas was determined with uncertainties of about 10% ($k = 2$).

In agreement with theory, similar values for the mutual diffusivity and the self-diffusivity were found. Furthermore, no detectable influence of the solute concentration on the mass diffusivities could be found by DLS and MD simulations within the narrow investigated mole fraction range between about (1 and 5)%. The broad range of mass diffusivities of the studied gas-liquid systems covering about two orders of magnitude from about (10^{-9} to 10^{-7}) $m^2 \cdot s^{-1}$ allow for developing structure-property relationships. Here, effects of the molecular weight and polarity of the various gases as well as the varying alkyl chain length of the solvents on the mass diffusivities are discussed. To further develop the intended prediction scheme, two additional classes of alkane-based solvents featuring the hydroxyl group – namely normal alcohols – as well as bulky charged structures in the form of ionic liquids will be studied in their binary mixtures with the aforementioned gases in a next step. In the same context, the DLS data will be used to test how reliably mutual diffusivities can be computed in MD simulations for the various fluid systems by different approaches.

Universal formula for the mean first passage time in planar domains

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We present a general exact formula for the mean first passage time (MFPT), $T(x_0)$, from a fixed point x_0 inside a planar simply connected domain Ω to a connected escape region Γ on the boundary $\partial\Omega$ [1]. The underlying mixed Dirichlet-Neumann boundary value problem is conformally mapped onto the unit disk, solved exactly, and mapped back (Fig. 1). The resulting formula (1) for the MFPT is valid for an arbitrary space-dependent diffusion coefficient $D(x)$, while the leading logarithmic term in Eq. (3) is explicit, simple, and remarkably universal. In contrast to earlier works [2], we show that the natural small parameter of the problem is the harmonic measure ω of the escape region, not its perimeter. The conventional scaling of the MFPT with the area of the domain is altered when diffusing particles are released near the escape region. These findings change the current view of escape problems and related chemical or biochemical kinetics in complex, multiscale, porous or fractal domains, while the fundamental relation to the harmonic measure opens new ways of computing and interpreting MFPTs.

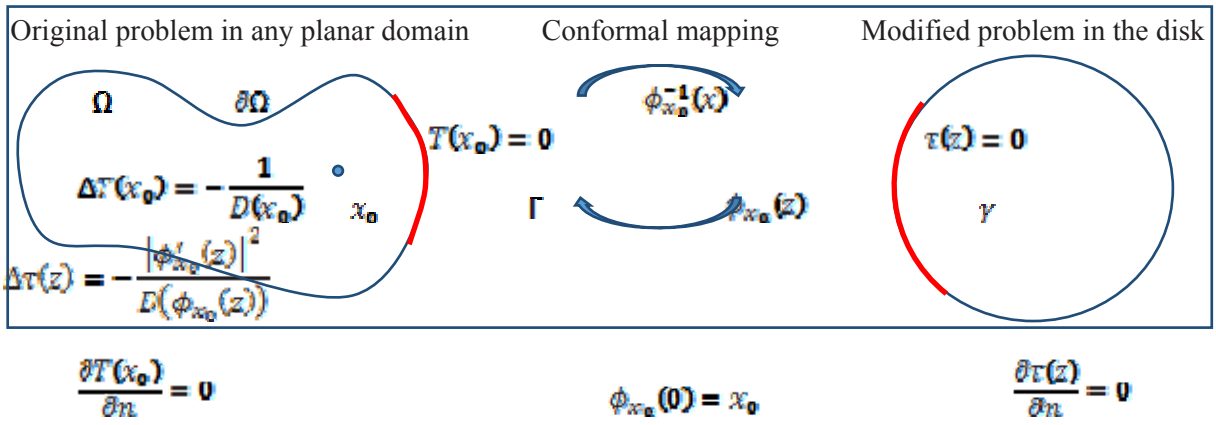

Figure 5: An arbitrary simply connected domain Ω (left) can be mapped onto the unit disk (right) by a conformal mapping $\phi_{x_0}(z)$ such that the origin of the disk is mapped onto the starting point x_0. The escape region Γ (in red) is mapped onto the arc $\gamma = (-\pi\omega, \pi\omega)$, where $\omega = \omega_{x_0}(\Gamma)$ is the harmonic measure of Γ seen from x_0.

The universal formula for the MFPT reads

$$T(x_0) = \int_\Omega \frac{dx}{D(x)} \left(-\frac{\ln|\phi_{x_0}^{-1}(x)|}{2\pi} + W_\omega\left(\phi_{x_0}^{-1}(x)\right) \right) \tag{1}$$

where

$$W_\omega(z) = \frac{1}{\pi} \ln\left(\frac{\left|1 - z + \sqrt{(1 - z\,e^{i\pi\omega})(1 - z\,e^{-i\pi\omega})}\right|}{2\sin\left(\frac{\pi\omega}{2}\right)} \right) \tag{2}$$

The asymptotic expansion of Eq. (1) over the natural small parameter, the harmonic measure ω, yields

$$T(x_0) = \frac{|\Omega|}{\pi D_h} \ln\left(\frac{1}{\omega}\right) + V_0(x_0) + V_2(x_0)\omega^2 + O(\omega^4) \tag{3}$$

where the explicit formulas for the coefficients $V_0(x_0)$, $V_2(x_0)$, ... are given in [1], and $D_h = \left(\frac{1}{|\Omega|} \int_\Omega \frac{dx}{D(x)}\right)^{-1}$ is the harmonic mean of the diffusion coefficient $D(x)$. The leading logarithmic term substitutes the conventional scaling $\frac{|\Omega|}{\pi D} \ln\left(\frac{1}{\varepsilon}\right)$ with the normalized perimeter ε [2].

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Spinodal decomposition of solutions during crystallization

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Motivation research: Explanation and prediction of the distribution of components in the crystallization solutions causes great difficulties. The modern theory of phase transitions cannot explain the results of many experiments of interphase mass transfer. One reason for this is the assumption that during crystallization the solution is in the metastable state. The decomposition of the solution occurs by binodal scenario in this case. Crystallization nuclei form and grow in solution. The purpose of this study to show that in many cases the solution during crystallization is in an unstable state [1,2]. The unstable condition leads to decomposition the solution by spinodal scenario. The unstable solution decomposes continuously in the whole volume in this case. The distribution component at the spinodal decomposition is determined by arbitrarily small perturbations of temperature or concentration.

Methodology & Theoretical Orientation: Experimental demonstration of spinodal decomposition of the solution is conducted video shooting process of decomposition of an aqueous solution of bromthymol blue while its crystallization. Locally - configuration thermodynamic model is used to explain the state changes of the solution during the phase transition [2,3]. This model allowed adding additional coordinate - mixing energy in the equilibrium phase diagram. Boundary of the spinodal area of the solution is built into the new coordinates. Spinodal defines curve the dynamic equilibrium that must be considered in the calculations of the processes of interphase mass transfer.

Conclusion & Significance: Spinodal decomposition of the solution explains the process of formation of a periodic distribution of the eutectic composites. The layer of the unstable solution is localized in front of the unstable interface. The unstable solution decomposes into phases, which have a composition close to the eutectic composition of the solid phases. The period of alternation of these phases is set by the period of instability of the interface [4]. Experiments show that the formation of dendrites in the mushy zone (Fig. 1) and extremum of the component concentration close to interface

also occurs in the spinodal decomposition scenario. The possibility of spinodal decomposition of the solution during its crystallization significantly alters the representation of interphase mass transfer. Many cases of the redistribution component during the phase transition cannot be explained without taking into account of spinodal decomposition.

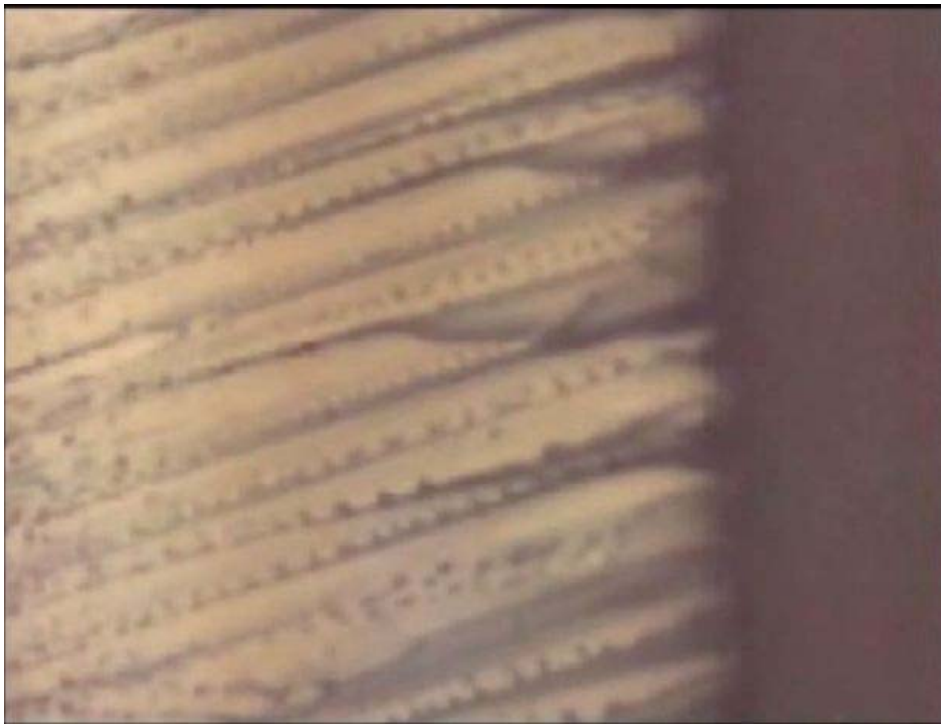

Figure 6: Formation of a dendrites branches at the borders of the eutectic structure under crystallization.

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Computer simulation of atomic complexes formation in grain boundaries

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For the molecular dynamics simulation of grain boundary selfdiffusion (GBSD) in Cu the embedded atom method (EAM) potential was used, obtained in [1], was used. The calculations were performed for the special grain boundary (GB) Σ5 (012)[100]. The mean square displacement (MSD) and GBSD coefficients were calculated. The results are in a good agreement with experimental results [2] and other results of computer simulation [3].

For description of grain boundary heterodiffusion (GBD) the next method was proposed. Into the model contained GB, close to GB symmetry plane, the marked M-atoms of hypothetical impurity were artificially added. These M-atoms are completely identical with other Cu atoms, but interact with the pair interaction energy Ea. After, the model was annealed for a long time at temperatures from 900 to 1200 K.

It was shown that for Ea=0.0 eV/atom MSD and GBD coefficients coincide with the GBSD values. For Ea=-0,2 and -0,5 eV/atom a decrease of MSD values and GBD coefficients was observed. It is supported, that such effect is connected with two reasons: the atoms moving from GB to the bulk and complexes formation from two and more atoms. The diffusivity of atoms in bulk, as well as diffusivity of the complexes are negligibly small. The "free" atoms move as in a pure Cu. Hence, a decrease of diffusivity is connected with a decrease of the movable atoms, but not with their mobility.

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Exploring fast diffusion at the nano-scale for nanojoining technologies

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With the continuing miniaturisation of micro-electronic devices the nanojoining technology is expected to become an enabling technology for the large-scale production of integrated components in the coming decades. The successful development of nanojoining processes requires fundamental understanding of diffusion, melting and phase formation at surfaces and interfaces at the nano-scale.

At Empa novel nanomultilayer (NML) joining materials are developed for fast, low-temperature nanojoining processes by exploiting short and fast diffusion paths along surfaces and interfaces [1]. Such NML fillers typically consist of alternating nanolayers (individual thickness < 10 nm) of a brazing metal/alloy filler (e.g. Ag, Cu, Ag-Cu) and a chemically-inert barrier material (e.g. carbon, nitride, oxide, refractory metal) and are deposited by magnetron sputtering techniques: see Fig. 1a.

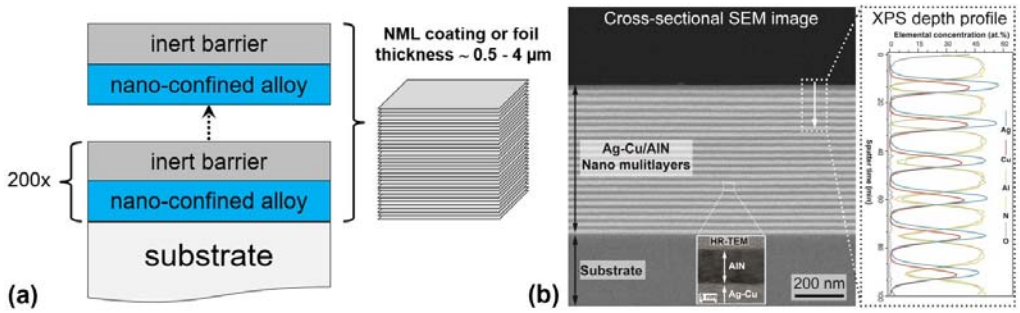

Figure 7: a) Schematic of the NML-filler, constituted of alternating nano-layers (thickness < 10 nm) of a metal or alloy (e.g. Ag, Cu, Ag-Cu) and a chemically inert barrier material (e.g. carbon, nitride, oxide, refractory metal). (b) Cross-sectional secondary electron image (light grey: Ag-Cu, dark grey: AlN) and corresponding composition-depth profile measured by XPS of an as-deposited Ag-Cu/AlN NML.

With the aim to exploit fast directional mass transport of the brazing material, the structural evolution of Ag/AlN and Ag-Cu nano-multilayers (NMLs), as deposited on α-Al_2O_3 substrates by magnetron sputtering, upon heating was investigated. A combinatorial analytical approach using real-time in-situ Synchrotron Transmission-X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Auger Electron Spectroscopy (AES) was applied to

study the structural and morphological changes of the NMLs during fast heating up to 550°C [2,3]. The experiments evidence fast transport of the metallic brazing filler to the NML surface at temperatures starting from 200 °C. The process is governed by the delicate interplay between spatial confinement, atmosphere [2], internal stress gradients [4] and the interfacial structure [5].

The investigations show that nano-confinement of metals and alloys in a NML configuration may be exploited to invoke fast directional mass transport at low temperatures for joining technologies.

Acknowledgment

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Adsorption und phase equilibria: completely without diffusion?

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If diffusion processes at interfaces are studied, adsorption can never be neglected. However, if adsorption at interfaces is studied, diffusion processes can absolutely be neglected – namely if we consider thermodynamic equilibrium states.

This is the pure theory. The question is to what extend the thermodynamic equilibrium is reached, especially as we know that the so-called "equilibrium state" is an abstracted idealized state allowing us to apply our theories for describing nature in a much simpler manner.

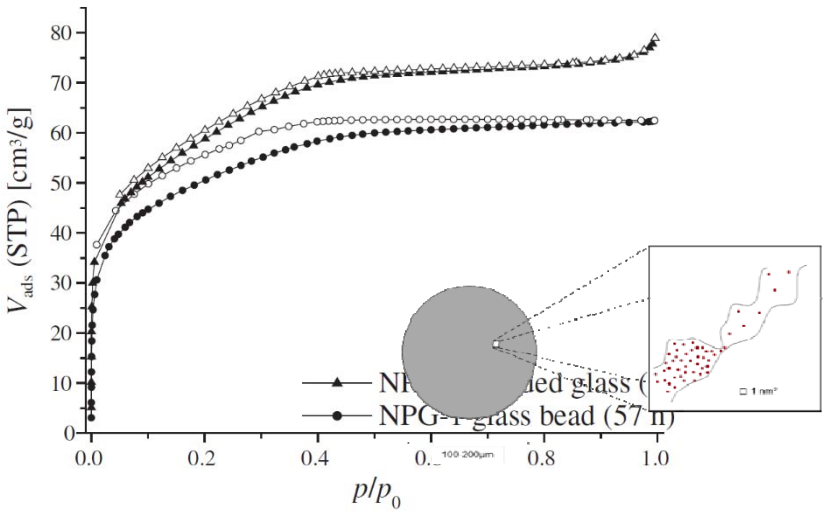

Figure 8: Nitrogen adsorption at 77 K on NPG-1 nanoporous glass beads (dots) and grinded NPG-1 nanoporous glass (triangles) with different measurement time (filled symbols: adsorption, empty symbols: desorption) [1].

In this work, we will present experimental and theoretical results concerning adsorption und phase equilibria being influenced by kinetic effects. This concerns experimental gas adsorption in nanoporous glasses with bottlenecks [1], carbonaceous adsorbents [2] or MOFs [3] as well as

calculations from gas adsorption isotherms [4] or liquid-vapor and liquid-liquid equilibria [5]. Additionally, recently built-up devices in our laboratory for measuring immersion enthalpies and the adsorption of liquid mixtures on porous solids by allowing to track the equilibrium time are shown.

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Lipids diffusion anomalies in bilayer membranes at main phase transition

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The diffusion coefficient jump by an order of magnitude at the liquidgel phase transition in the lipid membranes so far was missing theoretical description. Rattling in the cage microscopic mechanism of lipids self-diffusion responsible for the jump is captured by our microscopic model. We found analytically temperature dependencies of the major thermodynamic characteristics of the lipid membranes including diffusion coefficient, membrane thickness, volume per lipidmolecule. Dependence of phase transition temperature on lipid chain length is in quantitative agreement with experimental data.

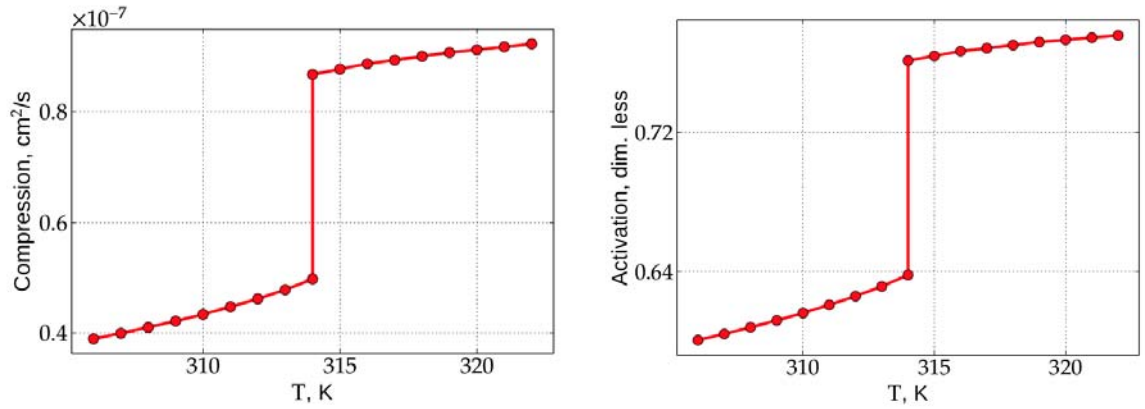

Figure 9: Separately plotted compression (left) and activation (right) factors contributions to the self-diffusion coefficient Eq.(1). At phase transition compression changes by two times, whereas activation contribution is relatively less pronounced All results are calculated using our previously developed microscopical model [1]-[3].

$$D = \underbrace{D(A_n)\exp\left(-\frac{A_n}{A-A_n}\right)}_{compression}\cdot\underbrace{\left(1+\frac{E_a}{k_BT}\right)\exp\left(-\frac{E_a}{k_BT}\right)}_{activation} \qquad (1)$$

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Effect of Ge addition in the thermal stability and microstructure Ag/Ge/AlN nano-multilayer system

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Nowadays, the development of new industrial nanostructured metallic filler materials for advanced low temperature joining applications requires a new approach to joints technology. Requirements move to reductions in joining temperature and time but also to improvements in the mechanical strength of the joint. The Nano multilayer systems were chosen to accomplish this task [1-5]. In this work the thermal stability and microstructure of the Ag/Ge/AlN nano-multilayer coating obtained by magnetron sputtering under different disposition conditions were investigated. The combinational approach to study the annealed coating, in Air and Ar atmosphere at 3 different temperatures (200º, 400º and 700 ºC) was carried out using HRSEM, XRD, in situ HT-XRD and RAMAN analysis. The first changes on the surface of the nano-multilayer were observed before fast annealing at 200°C in air atmosphere. BIAS application during the deposition of coating had a very strong influence on the morphology and structure of nano-multilayers due to the supplementary energy that allows Ag atoms to find the most opportune orientation. The presence of Ge slows down the outflow of Ag to the surface, owing to the solid solution formation at high temperature and higher surface diffusion during deposition as well as possible mixing between Ag and AlN layers The tensile stress induced by the Ge in the Ag layers was observed; unlike in the results in previous works [6-7].

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Non-isothermal diffusion in ternary systems: ground and microgravity experiments

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In multicomponent fluid mixtures subjected to a temperature gradient, the number of diffusion coefficients rapidly grows with the number of components. While binaries are sufficiently characterized by two coefficients, ternaries already require four independent diffusion and two thermodiffusion coefficients. Because of this increasing complexity, investigations of thermodiffusion (Soret effect) in truly multicomponent mixtures are scarce, although the latter represent the majority of practically relevant systems, ranging from simple liquids over colloidal dispersions to biological fluids.

Since there are two independent composition variables in a ternary mixture, two independent measurements are necessary to untangle the coupled diffusion and thermodiffusion processes. For this purpose we have developed a two-color optical beam deflection technique for the readout of the composition and temperature gradients in a Soret diffusion cell. The transformation of the signals from the refractive index to the composition space requires a precise knowledge of the optical contrast factors, the partial derivatives of the refractive index with respect to composition and temperature.

Driven by the unsatisfactory experimental situation, a joint international effort has led to the DCMIX microgravity project of the European and Russian space agencies ESA and Roscosmos. In the framework of DCMIX, three experimental campaigns have so far been conducted onboard the International Space Station ISS using different molecular model systems in a guaranteed convection-free setup. The experimental technique employed in the so-called SODI-instrument is two-color digital interferometry, which allows for a spatial reconstruction of the sample composition.

In this contribution both laboratory and microgravity experiments will be discussed. The results of a benchmark campaign have revealed a significant progress but also demonstrated the incompleteness of

our present understanding of the underlying physics and, to some extent, experimental difficulties. Some results for the Soret coefficients of ternary mixtures can qualitatively be interpreted on the basis of the so-called thermophobicity concept developed for binary mixtures, and they are in agreement with trends predicted by nonequilibrium molecular dynamics simulations.

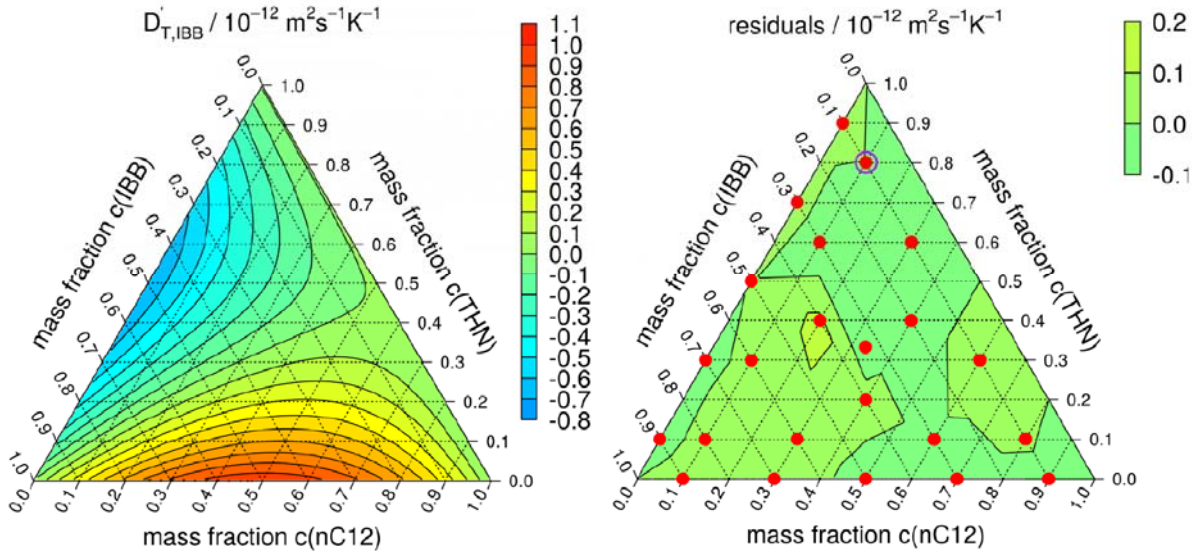

Figure 1: Left: Sign change of thermodiffusion coefficient of IBB in the ternary mixture dodecane/tetralin/isobutylbenzene (nC12/THN/IBB). Right: residues and compositions investigated

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Diffusion of immunological innovations in Russia at the turn of the 19th/20th century

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The 19th century was marked by the emergence of new disciplines such as bacteriology, immunology and hygiene and it was characterized by important research and international collaboration of scientists in Europe. The establishment of those disciplines was stimulated by the development of new methods and techniques in medical sciences und by fighting against infection diseases. The works of Louis Pasteur (1822-1895) formed a basis for the experimental immunology. His experiments with the fowl cholera let him not only develop a vaccine against it in 1880, but also discover a vaccine as the method of prevention against infectious diseases. The success of his first vaccines found a broad response in the scientific and public circles in different countries, including Russia [1].

The diffusion of the immunological innovations in Russia at the turn of the 19th-20th century proceeded at multiple levels. It was not only the acquisition of new techniques and know-hows, but also the transfer of objects (such as bacterial or vaccine strains). The knowledge exchange in practical contexts means an interaction between theoretical and applied studies. In immunology, as in other disciplines, new knowledge was often developed from the practical requirements, which in return produced new issues for the theoretical research. During the transfer process the local knowledge was acquired and then forced out. Thus the knowledge became at last international [2]. Because the transfer process of immunological research ran in both directions we can speak about diffusion or knowledge/scientific exchange rather then transfer, because transfer can go only in one direction. The current paper makes an attempt to analyze the diffusion of the foreign (French, German) innovations in Russia by discussing exchange practices and how successful they were.

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Wetting of grain boundaries in ultrafine-grained copper by liquid bismuth

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Severe plastic deformation is widely used for producing ultrafine-grained metallic materials. High-pressure torsion (HPT) processing results in high strength and homogeneous ultrafine-grained microstructure of the processed material. Such microstructures, however, exhibit poor thermal stability. Selective doping of the grain boundaries with impurities is one of the ways to stabilize the microstructure.

In the present work, we studied the effect of liquid Bi on the microstructure evolution of ultrafine-grained Cu at elevated temperatures. Cu polycrystals (mean grain size about 100 nm) were produced employing the HPT method. We characterized the microstructure of Cu samples subjected to post-deformation isochronal (1 h) annealings in the temperature range of 500 - 900 ºC, with and without the presence of liquid Bi.

The surface of the pure Cu and Cu-Bi samples annealed between 500 and 700 °C exhibits a bimodal microstructure, which implies the presence of ultrafine grains formed as a result of grain refinement during HPT, and much larger recrystallized grains with a size increasing with annealing temperature. The influence of Bi on the microstructure evolution of Cu polycrystals becomes evident after annealing at the temperature of 600 °C. The near-surface grains grow much faster in Cu-Bi samples than in pure Cu, which can be caused by Bi-induced increase of the grain boundary mobility and concomitant acceleration of grain boundary migration in Cu. The grain growth is accompanied by the penetration of liquid Bi and wetting of the grain boundaries. Partial and pseudopartial wetting occurs at the temperatures below 700 °C, whereas at higher temperatures a sharp increase of the fraction of fully wetted grain boundaries is observed. Micrometer-thick intergranular liquid phase layers penetrate into the bulk of the samples, preceded by the nanometric intergranular film of the Bi-rich phase (of 2-4 nm in thickness). Inclusions of Bi phase were not revealed in twin boundaries due to their lower diffusivity compared to that of random high-angle grain boundaries.

Thermodynamic activation energy for self-diffusion and order-order relaxation in intermetallic compounds: atomistic model and Monte Carlo simulations

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Self-diffusion and the 'order-order' relaxation process in intermetallic compounds is described in terms of effective atomic jump frequencies and the current degree of chemical long-range order. It is demonstrated that the thermodynamic activation energies of self-diffusion and the 'order-order' relaxation can be expressed in terms of the activation energies of more elementary processes. As the derived expressions differ from each other, the values of the thermodynamic activation energies for self-diffusion and the 'order-order' relaxation can be different although both processes are controlled by the same vacancy-mediated elementary atomic jumps.

In order to assess the the validity of the derived formulae different B2-ordering binary systems are simulated. The results of the computer experiments were in good agreement with the tested formulae. It was shown that the relationship between the activation energies observed in triple-defect B2-ordering binaries, where the value of the activation energy for order-order relaxations is substantially lower than that for self-diffusion, does not hold in the case of non-triple-defect binaries. Using the tested formulae, the origin of the effect was elucidated and attributed to the atomistic origin of the tendency for triple-defect disordering.

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Grain size influence on the release of radioactive isotopes out of target materials made of powder

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Radioactive ion beam production by Isotope Separator On Line method (ISOL) has motivated the construction of several nuclear facilities over the world [1]. The method consists in impinging solid target material with beams of stable nucleus. Radioactive nuclei produced during the collision are stopped in the target material and must diffuse out of it as fast as possible to transform them into ions before their radioactive decay. The release time must thus be as short as possible to avoid their losses. The release of the nuclei depends on several parameters, which are related to the chemistry of the atoms in the target matrix, to the geometry and micro-structure of the target, and to its temperature. In the case of targets made of grains, we assumed that an optimum grain size of the grains existed. To make possible an easy determination of the optimum grain size, we did not want to use numerical codes. Thus we have built an analytical description of the propagation of the atoms in the target material, while conserving the different physico-chemical parameters and avoiding the use of adjustable parameters. The description of the propagation process will be presented as well as the assumptions. Finally, the optimum grain size will be given.

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Unravelling intermittent features in single particle trajectories by a local convex hull method

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Many biological transport processes are intermittent [1, 2], with two or several alternating phases of motion. These phases can be distinguished by a change in their dynamical properties e.g. change in diffusivity, in drift, in autocorrelations, in distribution of increments or in dimensionality. Identification of such distinct phases is of major importance for describing relevant properties such as biochemical reaction rates, or biophysical mechanisms as translocation, transcription or drug delivery. This identification is challenging by two factors: the amount of experimental data is limited and different phases are not known *a priori*. We address the problem of identification of change points between distinct phases in a single random trajectory without prior knowledge of the underlying stochastic model.

We introduce two model-free estimators based on a local convex hull (LCH) constructed over trajectory points. The basic idea consists in considering a weighted *local* functional of the trajectory, $S(n)$, which depends on 2τ points around a point x_n. When applied to successive points along the trajectory, this local functional transforms the trajectory into a new time series, which can then be used to discriminate between different phases. The points x_n with $S(n)$ below some threshold are assigned to one phase while the remaining points are assigned to the other phase. We consider two functionals based on the local convex hull, the volume and the diameter (the largest distance in the hull).

Being based on purely geometrical properties of a trajectory, this method is sensitive to various changes in the dynamics and can be applied to a trajectory in any dimension. Its integral-like form makes it robust even in very noisy situations. We validate the LCH method by applying it to several models of intermittent processes. The recognition score R (the fraction of correctly recognized

points) was computed by averaging over 1000 independent trajectories. Figure 1 illustrates one example of heterogeneous diffusion, in which the particle diffuses in a composite medium with high and low diffusivities.

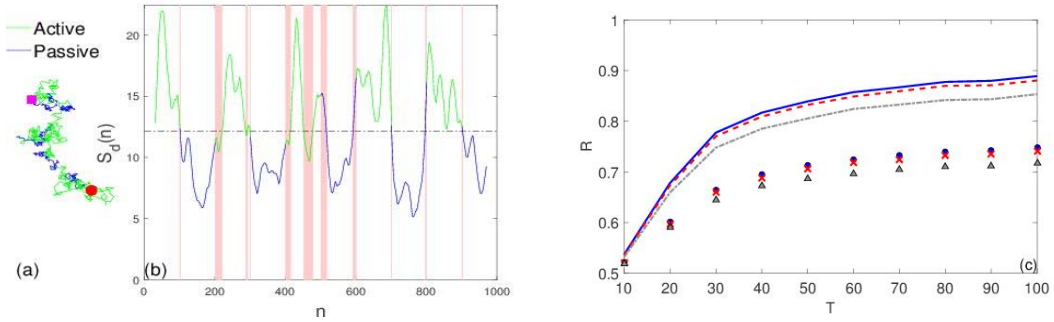

Figure 10: **(a)** A single trajectory with 1000 points of planar Brownian motion alternating a "slow" phase ($D_1 = 1/4$, dark blue) and a "fast" phase ($D_2 = 1$, light green), each phase duration $T=100$. **(b)** The weighted LCH diameter $S_d(n)$ with the window size $\tau = 10$, applied to this trajectory. Pink shadow highlights the false identification zones. Dashed horizontal line shows the empirical mean S_d over that trajectory. **(c)** Recognition score R of the diameter-based discriminator $S_d(n)$ as a function of the mean phase duration T. Lines show the results for the case $D_2 = 1/4$ with three noise levels σ_n: 0 (blue solid), $0.5\,\sigma$ (red dashed), and σ (gray dash-dotted) (σ being the empirical standard deviation of increments calculated for each trajectory). Symbols correspond to the case $D_2 = 1/2$ with the same levels of noise.

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Model-independent measurements of ATP diffusion in PEG-DA hydrogels with various mesh sizes

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Hydrogels are semi-solid polymer networks formed by cross-linked hydrophilic polymer chains, with mesh sizes that can be tailored by varying the concentration and/or the molecular mass of the polymers. Well-defined hydrogels are ideal materials for various applications including drug delivery, transport of nutrients, or devices to separate small molecules chromatographically. In this context, a fundamental understanding of the diffusion processes of solutes in hydrogels with different mesh sizes is important. A powerful tool to determine the diffusion coefficients of solutes directly, i.e. without the need of a fluorescent label and independent of any diffusion-model assumptions, is pulsed field gradient nuclear magnetic resonance (PFG-NMR). In this work, polyethylene glycol diacrylate (PEG-DA)-based hydrogels with mesh sizes ranging from 1.2 to 4.6 nm were prepared using polymers with molecular masses between 700 and 8000 g/mol and concentrations of up to 27%. The diffusion coefficients of adenosine triphosphate (ATP) in these hydrogels were studied by PFG-NMR. The correlation between the mesh sizes and the diffusion coefficients is analyzed and discussed.

Diffusive bending modes in bola lipid membrane of archaea

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We consider new diffusive mode and damping of the bending modes of the archaea membrane. One of the distinct properties of archaea is the presence of a special lipid in their structure - bolalipid. An investigation of the membrane of the archaea is interesting, first of all, because bolalipid membrane is found to be stable in extreme conditions: such as high pressure or high temperature, or very high/low acidity. This opens up potential applications of bolalipid membranes in e.g. medical and catalytic applications. The peculiarity of bolalipid membrane of archea is its intrinsically multi component content: bolalipid molecules can exist in two major configurations: integral shaped (O-forms) and hairpin shaped (U-forms). The U-forms surrounded by the O-forms cause local curvature of the membrane. An ability of bolalipids of the U-shape configuration to move within the bolalipid layer and nonequivalence of their potential energy in the regions of curved and flat membrane cause lateral diffusive flaws of U-forms in the flucruating membrane. For theoretical calculation of the bending modes of bolalipid membrane with small concentration of U-forms we take the energy functional for isotropic elastic thin plate Eq. (1) with dynamic nonzero local spontaneous curvature J_0. Motion of U-forms is described by Fick's laws in the presence of dynamic potential field effectively created by the membrane's bending. The bending is assumed to be small and cylindrical. The resulting system of self-consistent equations is solved by perturbation theory in the long-wavelength limit.

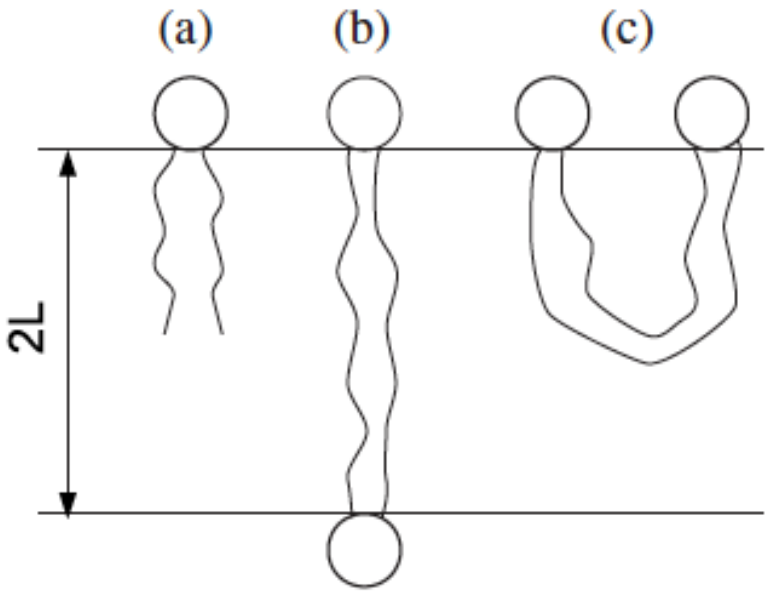

Figure 11: Schematic plot of lipid (a) and bolalipid O-form (b) and U- form (c). 2L is a thickness of hydrophobic region of the membrane. First microscopical model calculations of thermodynamic properties of bolalimid membrane were presented in [1].

$$W = \frac{Eh^3}{24\left(1-\sigma^2\right)}\int\left\{\left(\frac{\partial^2\varsigma}{\partial x^2}+\frac{\partial^2\varsigma}{\partial y^2}-J_0\right)^2+2\left(1-\sigma\right)\left(\left(\frac{\partial^2\varsigma}{\partial x\partial y}\right)^2-\frac{\partial^2\varsigma}{\partial x^2}\frac{\partial^2\varsigma}{\partial y^2}\right)\right\} \qquad (1)$$

Solving the system of self-consistent dynamic equations for the plate vibration coupled to U-forms diffusion we found two brunches of dispersion: purely diffusive brunch corresponding to U-forms motion and damped bending modes of the membrane's deviations from the flat conformation. Predictions for the spectral intensities of the membrane's fluctuations to be measured by e.g. neutrons scattering technique are presented.

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Drift mechanism of mass transfer on heterogeneous reaction in crystalline silicon substrate

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This work aims to study the pressure dependence of the thickness of the epitaxial silicon carbide SiC film growing from crystalline silicon Si due to the heterogeneous reaction with gaseous carbon monoxide CO [1]. It turned out that this dependence exhibits the clear maximum (Fig. 1). On further pressure increasing the film thickness decreases [2].

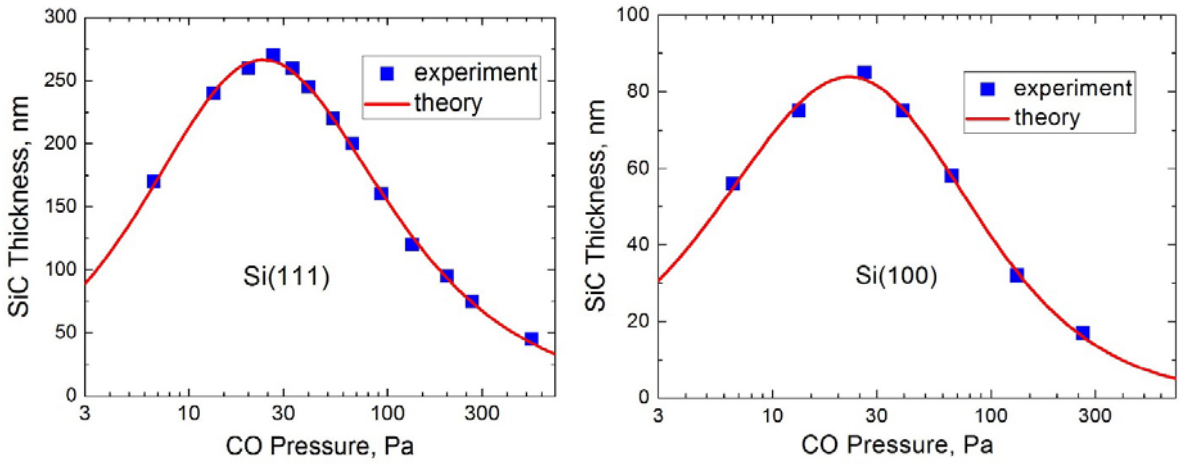

Figure 12: The measured dependences of the finite thickness of SiC film on CO pressure (squares) for Si(111) and Si(100). Solid lines are for theoretical dependences in the frames of the drift model, as obtained from Eq. (1).

As the growth mechanism, we suggest to consider the drift of molecules along the channels of the crystal which separates the gas-reagent and the zone of chemical reaction from the crystal-reagent, namely, CO and Si. The theoretical model has been developed which explains such a character of the dependence by the fact that the gaseous silicon monoxide reaction product inhibits the drift of the gaseous reagent through the channels of a crystal lattice, thus decreasing their hydraulic diameter. In the proposed hydraulic model, the dependences of the film thickness both on the gas pressure and time

have been calculated:

$$L_m(p_{CO}) = L_* \frac{4p_{CO}/p_*}{[1 + (p_{CO}/p_*)^n]^2}, \quad (1)$$

where L_m is the maximal thickness of SiC film, when it is no longer growing, p_{CO} is the CO pressure, n is the reversed index of polytrope, p_* and L_* are the parameters with dimensions of pressure and length, respectively. The dependence (1) of the film thickness on pressure contains only three parameters which could be determined from the best correspondence of formula (1) to the experimental data, using the least square method (see Fig. 1).

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Towards accurate diffusion measurements of slowly diffusing species

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NMR-based diffusion measurements are now extremely common place and are generally seen as the method of choice for measuring self-diffusion due to their non-invasive nature and general applicability including no specific concentration requirements, minimal sample preparation and speed. Further, as motion is measured over a specific timescale the NMR diffusion measurements can also report on geometries within which diffusion is occurring [1-3].

Most contemporary NMR spectrometers are now able to generate modest pulsed magnetic field gradients (e.g., gradient amplitudes $\leq$ 0.5 T m^{-1}) suitable for performing measurements on low viscosity/rapidly diffusing samples (e.g., $D > 1 \times 10^{-11}$ m^2s^{-1}) using predominantly ^1H as the probe nucleus with reasonably long relaxation times. The nature of the diffusion to be measured is normally a priori clear cut (e.g., isotropic or anisotropic, Gaussian or restricted). Such measurements are generally straightforward and typically make only modest demands on spectrometer performance and the gradient generation hardware. However, many samples of interest are by nature more viscous or even solid samples (e.g., solid phase electrolytes) with less initial certainty regarding the nature of the diffusion to be measured. Further, the probe nucleus may be a less favourable isotope than ^1H with an inherently much shorter relaxation time. Such measurements require special high current amplifiers and special NMR probes capable of generating high gradient pulses. Some commercial equipment is now capable of generating pulses in excess of 20 T m^{-1}. Performing measurements with such pulses can push a spectrometer to its performance limits such that it becomes difficult to separate artefact from reality and some aspects have long been recognised (e.g., ref. [4]). In fact, even the calibration of such equipment is not straightforward [5, 6].

This presentation details the complications of high gradient diffusion measurements, methods for obviating the problems and our progress in developing a protocol that will allow definition of a usable range of measurement variables (e.g., maximum gradient strength that allows reproducible results). Such a protocol would facilitate the comparison of results between different machines.

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The diffusion of law or borrowing from foreign legal systems

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The diffusion of law is transferring of the regulation from one legal jurisdiction into another.[1] The diffusion of law implies that the legal systems are dependent from each other where the entry of foreign legal norms into domestic law occurs to a certain extent spontaneously because of the interrelatedness of the legal institutions and the legal systems.

In the context of globalization, the cooperation between States on several important issues such as anti-corruption, international terrorism, legalization of proceeds of crime as well as interaction between legal and natural persons under economic treaty-based legal relations is essential.[2]

Therefore the diffusion of law is based on the implementation of standard rules and regulations of international law into specific national legal system in order to apply uniform institutions and the rule of law.

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Self-consistent molecular dynamics calculation of diffusion in higher n-alkanes

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Diffusion is one of the key subjects of molecular modeling and simulation studies. However, there is an unresolved lack of consistency between Einstein-Smoluchowski (E-S) and Green-Kubo (G-K) methods for diffusion coefficient calculations in systems of complex molecules. In this work [1], we analyze this problem for the case of liquid n-triacontane. The non-conventional long-time tails of the velocity autocorrelation function (VACF) are found for this system. Temperature dependence of the VACF tail decay exponent is defined. The proper inclusion of the long-time tail contributions to the diffusion coefficient calculation results in the consistency between G-K and E-S methods. Having considered the major factors influencing the precision of the diffusion rate calculations in comparison with experimental data (system size effects and force field parameters), we point to hydrogen nuclear quantum effects as, presumably, the last obstacle to fully consistent n-alkane description. The first results of the path-integral molecular dynamics will be presented.

The work was supported by the Russian Science Foundation (grant 14-50-00124).

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Grain boundary pseudopartial wetting

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Usually one distinguishes partial and complete wetting of surfaces or interfaces. In case of partial wetting contact angle $\theta > 0$ and the liquid droplet is surrounded by "dry" surface or interface. In the majority of cases the direct transition occurs from partial wetting into complete wetting, for example by increasing temperature or decreasing pressure. However, in some cases the state of pseudopartial wetting occurs between partial and complete wetting. In this case the contact angle $\theta > 0$, the liquid droplet does not spread over the substrate, but the thin (few nm) precursor film exists around the droplet and separates substrate and gas. Such precursor film is very similar for the liquid "pancake" in case of complete wetting and deficit of the liquid phase. The pseudopartial wetting has been observed before only for liquid/liquid mixtures (alcanes/water solution of salt or glucose) or Pb and Bi on the Cu surface. We observed the pseudopartial wetting of Al/Al grain boundaries (GBs) by solid Zn in the Al – 10 wt.% Zn ultra-fine grained polycrystals. The solid Zn partially wets Al/Al GBs (with non-zero contact angle). Nevertheless, the Al/Al GBs contain the 2 nm thin uniform Zn-rich layer connected with Zn grains. Such thin layers are the reason of high ductility of ultra-fine grained Al–Zn alloys at room temperature. This phenomenon opens the way for development of novel light-weight alloys. The pseudopartieal GB wetting by a liquid phase exists also in the WC–Co hard alloys. The pseudopartieal GB wetting by various liquid and solid phases also controls the properties of Nd–Fe–B-based hard magnetic alloys.

Diffusion Influencing on Competition between the Volume Solution and the Surface Segregation of Solved Elements in α-Fe

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Concentration of an element is a function of the tempering time after exposing and quenching from higher temperature, $X_b(t)$, described with the Langmuir curve and the Fowler theory accounting inter-atomic interaction in the segregation field [1] looks like a curve with the

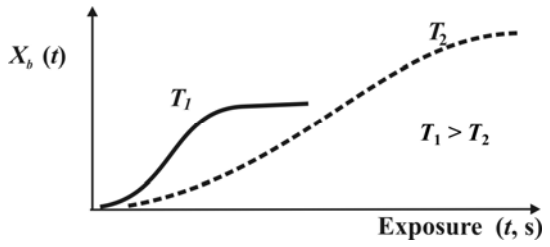

Figure 13: Surface segregations forming in solid solutions during isothermal exposing as a function on the time (t):

$$\frac{X_b(t)-X_b(0)}{X_b(\infty)-X_b(0)} = 1-\exp\left(\frac{FDt}{\beta^2 f^2}\right)\cdot erfc\left(\frac{FDt}{\beta^2 f^2}\right)^{1/2} \quad (1)$$

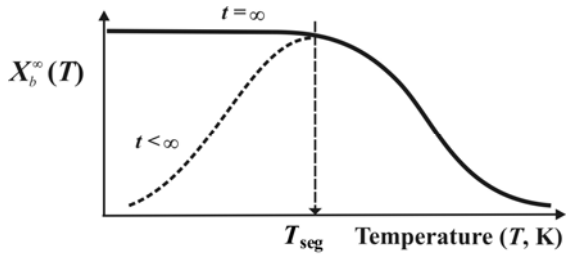

Figure 2: Equilibrium surface segregations $X_b^{\infty}(T)$ forming in solid solutions during isothermal exposing as a function on the temperature (T):

$$\frac{X_b^{\infty i}(T)}{X_{bo} - \sum_{i=1}^{N} X_b^{\infty i}(T)} = \frac{X_v^i}{X_{vo}^i(T)}\exp\left[\frac{-\Delta G^i{}_{seg}}{RT}\right] \quad (2)$$

saturation as that one in Fig. 1 presented by M.P.Seah in [1] as the equation (1). Another equation (2) proposed by M.P.Seah [1] was analyzed in this work and developed for multi-component systems, where the equilibrium concentration of the i-th component was represented as the temperature function $X^{\infty}{}_b{}^i(T)$: Fig.2. According to the above relationships (1), (2), the segregation rapidly reaches the equilibrium level under higher exposing temperatures, but its value is lower at higher temperatures than that one could be under lower temperatures. The latter was proposed in work [1] to be tied with the volume solubility increasing, as rule, under exposing temperature growth and being an opposite competitive process to equilibrium surface (interface) segregations formation. We proposed a certain temperature ($T_{seg}{}^i$) of observing a maximum segregation level for a solved element to exist. The value $T_{seg}{}^i$ in this work was determined mathematically from the maximum condition for relationship (2): $\partial X^{\infty}{}_b{}^i(T)/\partial T = 0$. We believed the following to be true at rather low

temperatures and enough long time period of the isothermal exposing: $X^{i}_{b}(T) \cong X^{\infty}_{b}{}^{i}(T) = const$. The segregation concentration ($X^{\infty}_{b}{}^{i}(T)$) and the limiting volume solubility ($X_{vo}{}^{i}(T)$) in (2) are functions on the temperature. Other parameters in (2) are assumed to be independent on the temperature. So, it was found the approximate solution of $\partial X^{i}_{b}(T)/\partial T \cong 0$ as

$$(T_{seg}{}^{i})^{2} = \frac{\Delta G_{seg}}{R}\left[X^{i}{}_{vo}(T) \Big/ \left(\frac{\partial X^{i}{}_{vo}(T)}{\partial T} \right) \right] \qquad (3).$$

It was experimentally shown, using Auger-spectroscopy method, that there is the certain temperature interval of forming the surface segregation of an element *i* solved in α-Fe (*i*=C, N, B, P, Mo, Ti, Al, S, Sn, Cu). The latter was experimentally observed as the temperature interval of preferential surface enrichment. The values of ($T_{seg}{}^{i}$) simulated with (3) are in rather good agreement with the obtained experimentally.

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Stochastic Kinetic Mean Field model - a new, low-cost, atomic scale simulation technique

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We introduce a new model for calculating the change in time of three-dimensional atomic configurations. The method is based on the kinetic mean field (KMF) approach [1], however we have transformed that model into a stochastic approach by introducing dynamic Langevin noise. The result is a stochastic kinetic mean field model (SKMF) which produces results similar to lattice kinetic Monte Carlo (KMC). SKMF is, however, more cost-effective and the algorithm is easier to implement. [2] The group made the software and the program code (together with tutorials) freely available to the scientific community at the http://skmf.eu webpage. We plan to keep this open source approach with the model's further developments, too. [3]

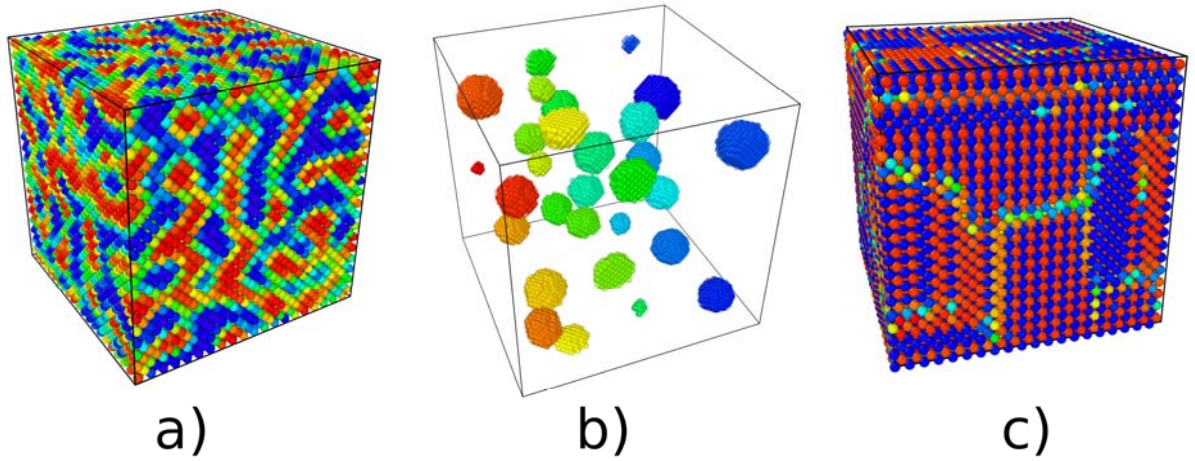

Figure 14: Demonstrations of a) spinodal decomposition, b) nucleation and growth and c) ordering in SKMF simulations

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Semi-analytical solutions of boundary value problems for the stationary diffusion equation in three-dimensional canonical domains

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We present the generalized method of separation of variables (GMSV) to solve boundary value problems for the stationary diffusion equation in three-dimensional canonical domains (e.g., parallelepipeds, cylinders, spheres, spheroids, ..., and also their combinations).

The main idea of the GMSV is as follows. For the sake of definiteness, consider diffusion in a domain outside N active particles of canonical forms (sinks). One looks for the classical solution (e.g., local concentration of diffusing particles) as a superposition of N implicit expansions into basis solutions of the diffusion equation given in each curvilinear coordinate systems attached to the centers of the sinks. The unknowing coefficients of the linear combination are fixed according to Robin boundary conditions by using addition theorems to re-expand the basis solutions in one local coordinate system on the appropriate basis solutions in another local coordinate system. Although the numerical computation of the coefficients involves a matrix inversion, the use of the basis solutions specifically adapted to the symmetries of each geometric element makes the GMSV particularly efficient, especially for exterior problems. Thus, the corresponding boundary conditions are exactly satisfied by simple substitution accompanied by the use of appropriate addition theorems. As a result, the original boundary value problem with respect to a local concentration of diffusing particles reduces to resolving second kind infinite system of linear algebraic equations (ISLAE) in the Hilbert spaces of sequences. Provided the relevant matrix operator of the ISLAE is compact, the system can be truncated and numerically solved as justified by the reduction method. Moreover, we show that for some configurations of sinks the resolving ISLAE can be solved by iterations.

As an important example, we discuss the detailed description of the GMSV for an arbitrary configuration of non-overlapping partially reactive spherical sinks.

As an application of the method, we obtain the Green function that is the key ingredient to determine various characteristics of stationary diffusion such as reaction rate, escape probability, harmonic measure, residence time, and mean first passage time, to name but a few. The relevant aspects of the numerical implementation and potential applications in chemical physics, heat transfer, electrostatics, and hydrodynamics are discussed.

Analysis of diffusion in porous media using a porous graph approach

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Solute transport and diffusion in porous media is a long standing problem [1]. The general random walks framework has been shown to describe quantitatively the anomalous transport patterns frequently observed in fractured and heterogeneous porous media [2]. One of the major conceptual difficulties consists in a very broad range of time and length scales in the dynamics that prohibits using conventional theoretical approaches or numerical simulation methods. To overcome this problem and bridge various scales, we suggest to represent a porous medium by an equivalent "porous graph" (Fig. 1, see also [3]) and then to model the complex dynamics of a particle in the porous medium by a continuous time random walk (CTRW) on that porous graph. The graph structure accounts for the inter-connectivity of pores, whereas their geometric properties (shapes of pores and of connectivity regions) are, to some extent, captured through the CTRW characteristics, hence connecting the topological and dynamical properties of the system.

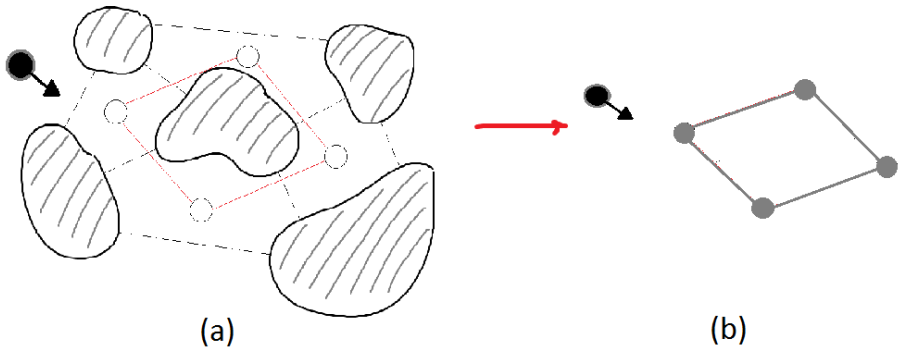

Figure 15: Diffusion of a particle in a porous medium (a) is modeled by a continuous time random walk on a porous graph (b).

In our CTRW approach, the space and time characteristics of individual jumps on a graph are coupled that requires developing new theoretical tools. We present several preliminary results on the long-time asymptotic behavior of a particle on a porous graph. To validate the proposed coarse-graining scheme, we compare the asymptotic behavior of the CTRW on a porous graph with the original continuous dynamics in several models of porous media. In particular, we investigate how shapes, sizes, and inter-connectivity of pores can affect the long-time behavior.

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How to model language diffusion

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We discuss the application of physics to the study of language spread: Can language diffusion be modelled by techniques used in solid state physics?

Many of the world's around 6000 languages are in danger of disappearing as people give up use of a minority language in favour of the majority language in a process called language shift. Language shift can be monitored on a large scale through the use of mathematical models by way of differential equations e.g. reaction-diffusion equations. We proceed in a different way: we propose a model for language dynamics based on the principles of cellular automata and combine it for the first time with very detailed empirical data. We note, however: Only when empirical data over a certain time and space scale are available and

used for calibration can the strength of this method be fully. Cellular automata models can be used even in cases where models based on differential equations are not applicable e.g. in situations where one language has become dispersed and has retreated to language islands. Using data from a bilingual region in Austria, we show that the most important factor in determining the spread and retreat of a language is the interaction with speakers of the same language.

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Diffusion of environmental awareness: experience from Russia

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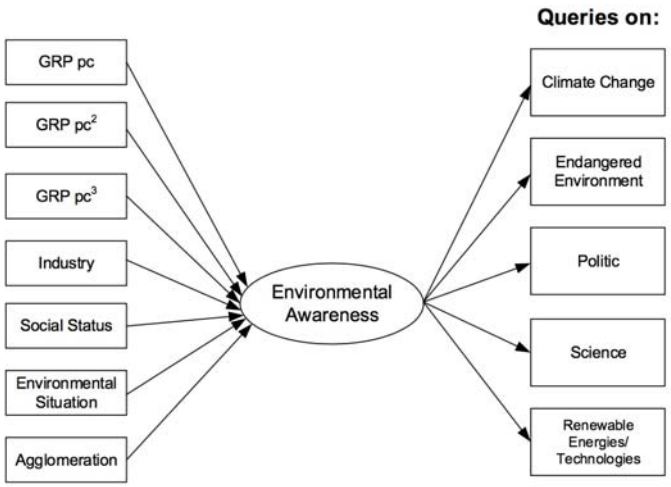
In December 2015, the parties to the Kyoto Protocol reached an agreement for reducing anthropogenic greenhouse gas emissions – after years of negotiations. The success of this agreement depends substantially on the willingness of the participating countries to realize their "Nationally Determined Contributions". A high level of "environmental awareness" in the population will certainly affect this willingness in a positive way. The necessity arises, to investigate the diffusion of "environmental awareness", and also the (economic) factors, on which this diffusion depends.

This paper addresses these questions for the regions of the Russian Federation. The 82 regions are sufficiently diverse regarding cultural and economic issues, such that interesting conclusions can be expected. Moreover, Russia is still among the largest emitters of greenhouse gases in the world.

A relevant question refers first to the abstract concept of "environmental awareness" itself: how to define it? how to measure it? We make use of the "Multiple-Indicator-Multiple-Causes" (MIMIC) approach, which is based on a variety of indicators for environmental awareness and a variety of causes, potentially influencing this awareness. In our model the indicators ($y_1,\ldots,y_n$) are queries of relevant environmental phrases from the Russian internet search engine Yandex. In addition, observable "causes variables" ($x_1,\ldots,x_m$), such as the gross regional product per capita (GRP pc) are needed to explain the latent variable η, the environmental awareness.

We thus obtain the following path diagram illustrating the MIMIC model with the specifications of the causes and the indicator variables:



The goals of the paper are now to provide information on the status and the development (diffusion) of the environmental awareness in the Russian regions in the following sense:

a) The diffusion of environmental awareness η^R_t in region R of the Russian Federation over a period of years t.

b) The dependence of the diffusion on the level of GRP per capita: $\eta^{R}_{t} = \eta^{R}$ (GRP^{R}_{t}pc); this corresponds to the idea of an environmental Kuznets Curve.

c) The ranking of the Russian regions according to the level of environmental awareness and the changes over the periods of time.

The results will therefore allow some insight into the diffusion of the concept of "environmental awareness" depending on the economic development in the various regions of the Russian Federation.

Reconstruction of a focused e-beam profile in amorphous carbon using diffusion of n-alcane molecules along carbon nanopillar sidewalls

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Electron beam induced deposition (EBID) is a versatile technique used to fabricate nanometer structures on solid substrates [1]. Carbon dots and pillars can be grown on various substrates in a scanning electron microscope in the presence of residual hydrocarbons.
To date, mapping of e-beam intensity in a target is performed mostly by simulation. Here we propose an alternative approach in which the layer of adsorbed hydrocarbon molecules diffusing along the pillar serves as a medium sensitive to the spatial distribution of fast electrons penetrating the target.
Solution of the mass transport equation in cylindrical coordinates *r, z* relates the molecule concentration *C* with the current density *j* and the diffusion coefficient *D*. On a conical tip Cj = const, while *C* is proportional to r^2. The cone angle grows with the beam current *I*. Increasing *I* by steps produces a series of *j versus (r,z)* plots at various scattering angles.
The typical pillar shapes are compared with calculated equi intensity contours in Fig1.
Measurements of the pillar growth rate give insight into dynamics of molecular motion and pinning. We have estimated $D \sim 10^{-8}$ cm^2/s at $T \approx 300$K and consider decane as the most probable species responsible for material delivery to the growing tip. We suppose that the surface roughness rather than the atomic arrangement is a crucial factor determining mobility of long C-H chains.

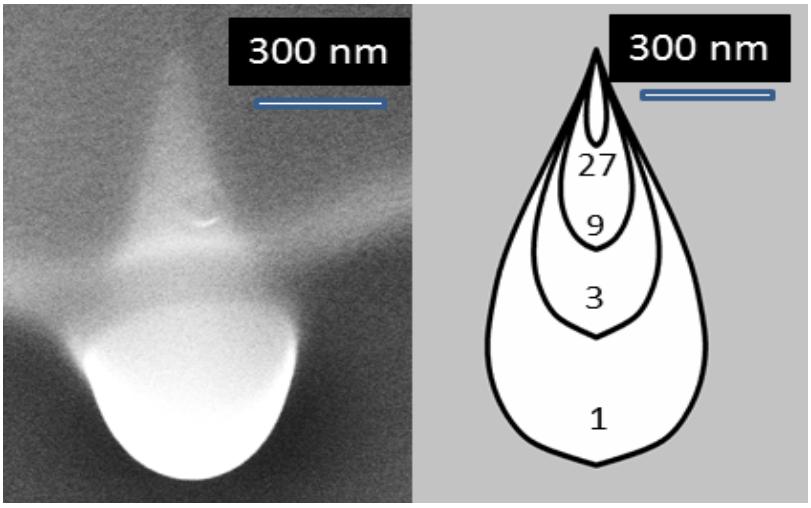

Figure 16: Left: pillars grown on two sides of amorphous carbon film irradiated by a focused 20 keV electron beam; view from the backside, tilt 45^0 . Right: calculated contours of equal current density; figures indicate scattered intensity in arb.units

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Effect of the impurity on diffusion creep of dilute Cu-based solid solutions

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We analyzed change in diffusional creep polycrystalline copper, depending on the impurities dissolved therein. Data were used on strain rate at high temperatures (> 0.85Tm) and low stresses (<0.5 MPa), obtaining in zero creep experiments. In dilute solutions, the creep depends on the surface activity of the impurities and their ability to affect the bulk diffusion of alloy. In general, at low concentrations of surface active impurities creep rate falls. This is due to a decrease in the effectiveness of interfaces (free surfaces and grain boundaries) as sources and sinks of vacancies. Increasing the concentration of the second component leads to change in the rate of bulk diffusion of solid solution. Accelerating the bulk diffusion entails a reduction in the viscosity, slowing down - increase viscosity. Thus, the diffusion creep in dilute solid solutions can be accelerated with increasing concentration, decelerated and had extreme behavior (decrease and then increase the creep rate).

Posters

Complex structures in the Au – Cd alloys: electron origin of diffusion ordering

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In the Au–Cd alloy system there is a large number of the intermediate phases. This is due to the substantial increase in effects of ordering and the contribution of the band structure energy of valence electrons. The classical example of the diagram with the Hume-Rothery phases is the Cu – Zn diagram and related diagrams. Few and relatively simple phases in Cu–Zn change to structurally complex compounds in Au–Cd. The structures of Au–Cd compounds can be combined into groups according to their relation to the high-symmetry structures: Au_3Cd-*tI*16 is related to *fcc*; phases AuCd-*mP*6, *oP*4 and *hP*18 are related to *bcc*. Au_5Cd_8-*cI*52 and $AuCd_3$-*hP*24 can be considered as structures derived from *bcc* with superlattices and vacancies. Several compounds have separate phase regions and are defined by the formation of the tetrahedral, icosahedral and trigonal-prismatic clusters such as in Au_3Cd_5-*tI*32, $AuCd_2$-*mC*72 and $AuCd_4$-*hP*273. The latter phase provides an example of a complex structure forming an almost completely spherical Brillouin zone (BZ) polyhedron accommodating the Fermi sphere (FS).

By constructing the BZ-FS configurations [1] for the Au–Cd compounds we can see the complex polyhedra with the BZ planes touching the FS that demonstrates significance of the band structure energy of valence electrons for the phase stability [2]. The driving force to form a variety of diffusion ordering superlattices in the Au–Cd alloys can be understood as an advantage of the band structure energy over the electrostatic energy. Additional BZ planes that arise due to formation of the ordered supercells lead to formation of many-faced polyhedra that accommodate well the free-electron Fermi sphere.

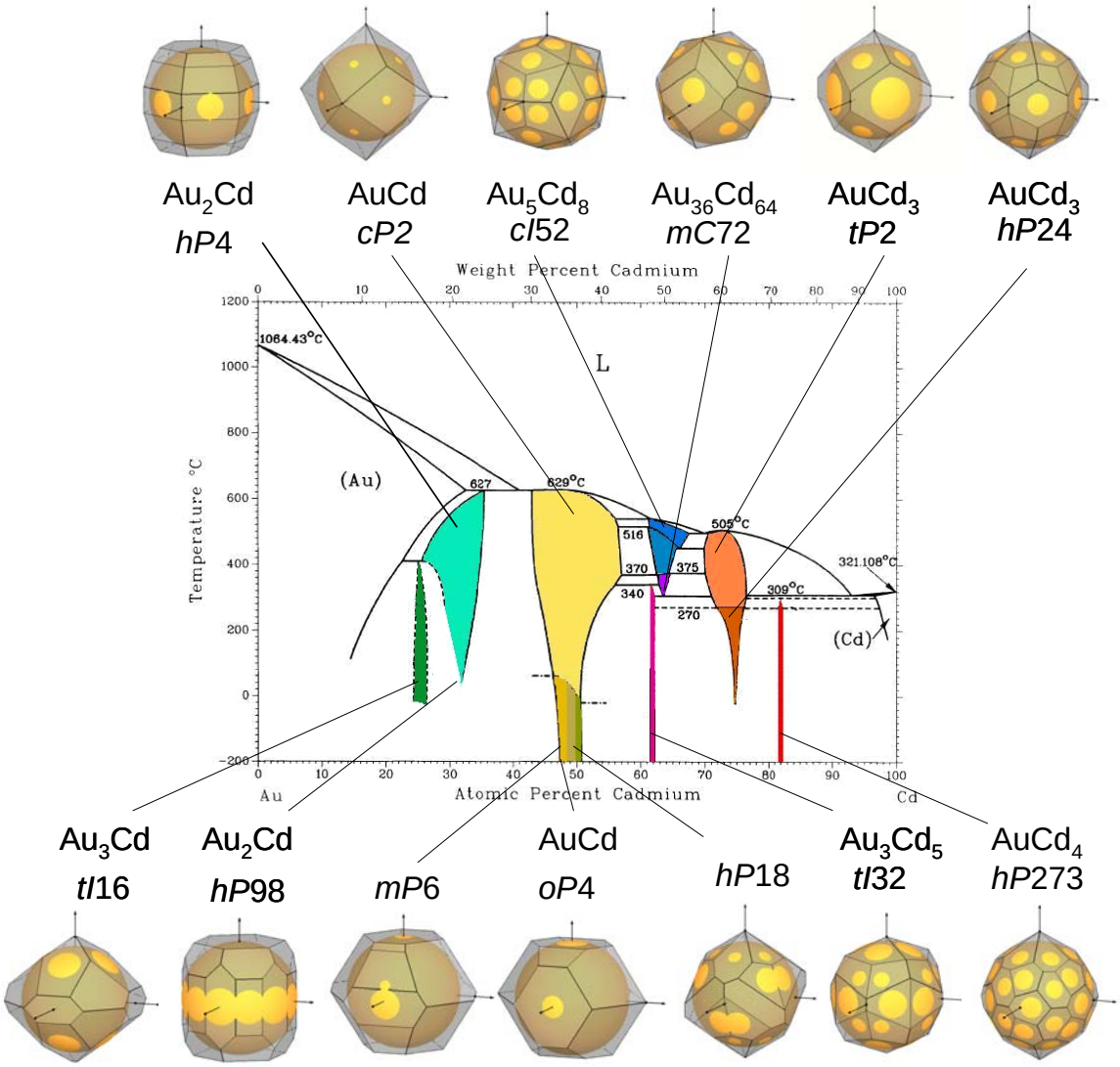

Figure 17: Au – Cd phase diagram. Constructions of FS-BZ configurations are shown for the intermediate compounds with indicated compositions and structure types.

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Precipitation and dissolution in melt-grown GaSe crystals doped with sulfur or rare-earth metals

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The layered semiconductors, GaSe crystals are grown from melt for laser optics. We have developed a technique, which provides structurally perfect, stoichiometric GaSe crystals [1]. This material gets more and more interest as a crystal for nonlinear optics, since it can work as a frequency converter in IR and THz ranges. In this connection it is important to use isovalent and non-isovalent doping elements to enhance efficiency of second harmonic generation (SHG). Therefore, an idea was considered to use isomorphic small sulfur atoms for doping. Light doping with S from 0.01 to 0.5 at.% improved GaSe optical properties [2]. We have studied the range of sulfur doping from 0 to 100 at%. All materials were first synthesized and then crystals were grown from melt in argon atmosphere. We used XRD to analyze phase composition of the grown crystals. The diffraction patterns show presence of just one phase in all cases. Shifts of peaks point to the fact that all sulfur dissolves in GaSe. The calculated unit cell parameters shows linear character of concentration dependence typical of regular solutions. Measured optical and photoluminescence spectra have shown increase in band gap width and shift of fundamental absorption to blue edge as well as increase in PL intensity with increase in sulfur content.

A new approach to enhancement of nonlinearity of GaSe crystals is doping them with Er. It occurs that doping with erbium can improve optical properties, but erbium dissolves weakly and forms precipitates, which brings to light scattering [3]. Most precipitates are high-melting ErSe particles. We made an effort to avoid formation of these particles and to increase solubility of Er in GaSe moving to metastable state via development of synthesis and cooling conditions, which proved to be sensible, since we reached up to 0.3at%Er solubility for the $Ga_{0.99}Er_{0.01}Se$ initial composition, which is by an order of magnitude higher than in the melt-grown Er-doped GaSe reported in [3]. Temperature

gradient in the furnace has a considerable effect on phase state of synthesized crystals. The crystal quenched from hotter zone contains just solid solution, while the crystal from cooler zone contains solid solution with the same unit cell parameters and a small amount of Er_2Se_3 phase, which was confirmed both by XRD and EPMA measurements. There is a SEM image in secondary electrons showing these particles in Fig. 1b. To continue our study of precipitation and solution of doping elements, we are going to grow GaSe:Er from melt using the synthesized material in order to homogenize Er distribution and improve crystallographic perfection of the synthesized polycrystals, which contain a lot of stacking faults due to disordered growth of domains in (0001)plane.

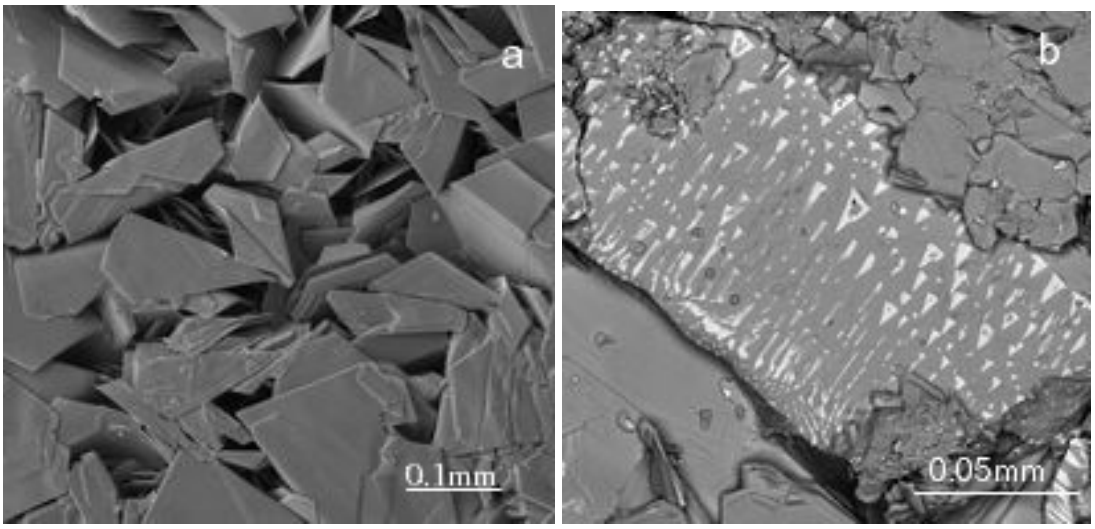

Figure. 1. SEM images of GaSe:Er synthesized crystals: (a) hot zone; (b) cold zone

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Model of grain boundary diffusion in titanium and zirconium α- and β-phases

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Titanium and zirconium are advanced construction materials widely used in nuclear industry and extensively applied in medicine. Both metals are characterized by abnormally low values of grain boundary diffusion activation energy Q_b in low-temperature α-phase. Expressed in dimensionless form Q_b/kT_m (k – Boltzmann constant, T_m – melting temperature), these values are 6 and 7 for titanium and zirconium respectively. These values are below respective energies typical of single-phase metals such as copper and aluminum (9 and 10 respectively), and grain boundary diffusion activation energy Q_b in high-temperature β- phase which is 9.5 kT_m for titanium and 10 kT_m for zirconium. Currently there is no model describing any reasons for abnormally low values of grain boundary diffusion activation energy in titanium and zirconium α-phase.

Paper [1] suggests a phenomenological theory of nonequilibrium grain boundaries (TNGB) which allows calculating Q_b values in pure metals which are lacking any structural transitions. Proceeding from this theory, the boundary consists of islets of 'amorphous' and 'solid' phases. The ratio of the volume fractions of these phases is proportionate to the free volume of the boundary. The process of grain boundary diffusion is triggered by fluctuations of structural amorphization or 'melting' during which 'corridors' appear in the boundary between islets of the 'amorphous' phase along which diffusion transfer occurs. Thus, the grain boundary diffusion activation energy appears to be related to the volume fraction of the amorphous phase islets and consequently to the free volume of grain boundaries. The theory carefully describes diffusion processes in single-phase materials, however, it is inapplicable to calculate parameters of grain boundary diffusion in titanium and zirconium, because these metals at elevated temperatures experience polymorphic transformation the thermodynamics of which affects the kinetics of heterophase amorphization fluctuations.

Based on generalization of TNGB approaches, the paper suggests a theory of grain boundary diffusion in metals undergoing phase transitions. Thermodynamic parameters of these fluctuations were calculated and self-consistent phenomenological models of boundary structures in α- and β-phases were suggested. Abnormally low values of the grain boundary diffusion activation energy in low-temperature titanium or zirconium α-phase are explained by contribution of additive components associated with the release of energy in phase transformations to the free energy of heterophase amorphization fluctuations. Values of the grain boundary diffusion activation energy in titanium and zirconium α- and β-phases that were obtained on the basis of the developed model with a high degree of accuracy conform to the experimental data.

The research was performed with the support of the Russian Science Foundation (grant No. 16-13-00066).

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Phenomenological theory of diffusion in metal oxides and ceramics

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Diffusion in metal materials is researched thoroughly today both experimentally and theoretically. However, the issue of theoretical description of diffusion processes in ceramics, including metal oxides, remains understudied. It is crucial to note that in order to build a model to calculate parameters of bulk diffusion in ceramic materials, it is important to take into account some features of their structure and properties.

The first feature is the so-called 'loose packing' of ceramic crystalline structures as compared to metals (lower packing index). This provides additional opportunities for diffusion jumps of atoms, including jumps of lattice atoms to an interstitial space, while in close-packed metals jumps between interstices are more energetically justified for nonmetal atoms that have much smaller radius in the metal lattice as compared to metal atoms. Thus, ceramics offer an opportunity of atom diffusion both in line with the vacancy mechanism and interstitial mechanism.

The second feature is that unlike metals, the crystalline structure of ceramics consists of several kinds of atoms: in oxides it consists of oxygen ions and metal ions that have comparable activation energies. Although oxygen ions are usually smaller in size than metal ions, both oxygen and metal are equal participants in the diffusion process.

The third feature is the lack of the diffusing particles charge shielding effect typical of metals. Oppositely charged ions are generally taken into account by describing the structure of ceramics with two sublattices (oxygen and metal) and by describing jumps of ions to their vacancy: oxygen ions jump to 'oxygen vacancies', while metal ions jump to 'metal' ones.

The fourth important feature characterizing the structure of oxide ceramics crystalline lattices is that it has a strong concentration of structural vacancies and significant deviations from the ideal stoichiometry, which has a significant impact on the diffusion properties of ceramics.

Another specific feature of ceramics is an opportunity to combine two kinds of ions (oxygen and metal) and form a variety of different compounds and structures. This creates extra opportunities to carry out several bulk diffusion scenarios especially in case of violated stoichiometry.

The paper presents a phenomenological description of bulk diffusion in oxide ceramics. Ideas described in [1] are underlying the theory currently considered in this research. To describe elementary diffusion processes in metals, this paper proposes two main scenarios: 'liquid corridor' model and 'empty corridor' model. In the first model, the diffusion jump of an atom to a vacancy is described as diffusion in a fluctuatingly emerging 'melt corridor' that links the point where there is an atom with the point where there is a vacancy. In the 'empty corridor' model, diffusion occurs as a result of vacancy-free movement of an atom inside a fluctuatingly emerging cavity that links a diffusing atom with the nearest vacancy.

The paper considers vacancy and vacancy-free diffusion models. In case of vacancy models, the ion migration process is described as a fluctuation with the formation of a 'liquid corridor' along which the diffusion ion transfer in a 'melt' is performed, or as a fluctuation with the formation of an 'empty corridor' in which the ion motion proceeds without activation. The vacancy-free model considers fluctuation with the formation of a spherical liquid region the size of which corresponds to the first coordination sphere. It has been shown that both the vacancy models work well in cubic metal oxides and the vacancy-free model is effective for describing diffusion in oxides having a noncubic structure.

Detailed comparison of the proposed models with the experimental data has been performed. It has been shown that the values of the activation energies for diffusion of metal and oxygen ions agree well with the published data on bulk diffusion in stoichiometric oxide ceramics.

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Influence of heat treatment on magnetic properties of Cu-Sn-Co-based materials produced by powder metallurgy

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In the foundation of this work is the issue for production of non-magnetic materials with predetermined weak magnetic properties. Preferable solution is to dope these materials with ferromagnetic impurities in low concentrations. One of the efficient ways to obtain such materials is the use of powder metallurgy which gives an opportunity to produce complex powder compositions with variety of components in precisely specified concentrations.

As an research object powder compositions of systems Cu-Sn (8 wt. % Sn) and Cu-Sn-P (8 wt. % Sn; 0,5 wt. % P) with the addition of 1,5 wt. % Co were chosen. After mixing and pressing all samples were heat treated at 800 ˚C with different cooling rates.

Noticeable solubility of components in Cu-Co system is observed at high temperatures [1]. This fact makes it possible to form specified magnetic properties only by formation of metastable solid solution with the further annealing in order to exclude Co particles from Cu (reduce Cu concentration in Co solid solution) and change the quantity of ferromagnetic domains in material [2]. Experimental results in this work with fast cooled Cu-Sn-Co system samples showed the same except there was no solubility of Co in Cu-Sn matrix. Anyway Co-Cu solid solution formation reduces sample magnetization in comparison with the pressed one. Formation of Cu-Sn-Co solid solution was discovered only after Cu_3Sn chemical compound started to grow due to lower cooling rates. In the second case saturation magnetization became lower than for fast cooled sample because diffusion of Co into Cu-Sn solid solution was appeared and consequently the amount of ferromagnetic Co decreased.

In the fast cooled samples of Cu-Sn-P-Co system besides the partially dissolution of Cu in Co diffusion of phosphorus in Cu-Sn matrix with further formation of Co_2P chemical compound was occurred. Presence of cobalt phosphide decreased magnetic properties drastically because of paramagnetism of Co_2P [3]. In slow cooled samples additional phase of eutectic copper phosphide Cu_3P was discovered and saturation magnetization rose. Investigation of samples with various cooling rates proved that with the formation of tin-rich phase caused the dissolution of Co_2P with simultaneous diffusion of phosphorus to the boundaries of Cu_3Sn phase and formation of Cu_3P.

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Calculation of the vacancy diffusion rate: beyond the NEB precision

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Migration of point defects determines many microscopic processes in nuclear materials: climbing of dislocations, diffusion of fission products, formation of bubbles and swelling. Experimentally measured self-diffusion is a combination of effects of vacancies and interstitials, but in bcc metals the impact of vacancies is much higher. Calculation of the vacancy diffusion rate is important for building a mesoscale model of the evolution of fuel in reactor conditions. The generally accepted model for temperature dependence of diffusion of defects is the Arrhenius equation $D = D_0 \exp[-E_a/k_B T]$, where E_a is a free energy barrier and D_0 is a frequency factor, determining an effective frequency of jump attempts [1]. The most common method to obtain the energy barrier in molecular dynamic simulation is Nudged Elastic Band method [2]. However, the question of the accuracy of the NEB remains open. In particular, there is a question of delayed relaxation of the jumping atom environment, and consecutive effects on the mobility of vacancies [3]. This fact is considered as evidence that the NEB can give the reaction path different from the real one. The NEB method is also not applicable in cases when the lattice is unstable at zero temperature, e.g. bcc lattice of uranium [4].

This work shows that the molecular dynamic simulation of the motion of defects in bcc metals gives the result different from the NEB prediction. Temperature dependence of the migration energy is discussed, and the method for the accelerated calculation of this dependence is considered.

The work is supported by the Russian Science Foundation (grant 14-50-00124).

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Driven mixture of active/passive colloids in a constricted geometry

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Characteristics of a driven binary colloidal mixture are explored. The mixture is confined to a two dimensional narrow channel and consists of both active (self-propelled) and passive particles. The channel walls are hard and periodic boundary condition is applied along the channel. Colloidal particles perform Brownian motion in a solvent having a fixed temperature and interact with each other via a Debye-Huckel Coulombic interaction (Yukawa potential). A constant external force drives one of the species along the channel. Hydrodynamic interactions are neglected and the dynamics is assumed to be over-damped. The flow increases nonlinearly with the external force but does not exhibit a notable dependence on channel width. Above a critical driving force the system undergoes a homogeneous to laning transition. It is shown that the mean lane width as well as the laning order parameter increases with the channel width. We investigate the dependence of laning parameter on various quantities namely the number ratio of active to passive colloids, the magnitude of the externally driving force etc.

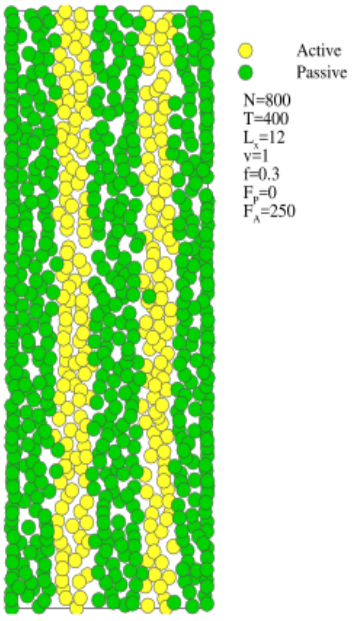

Figure 18:lane formation.

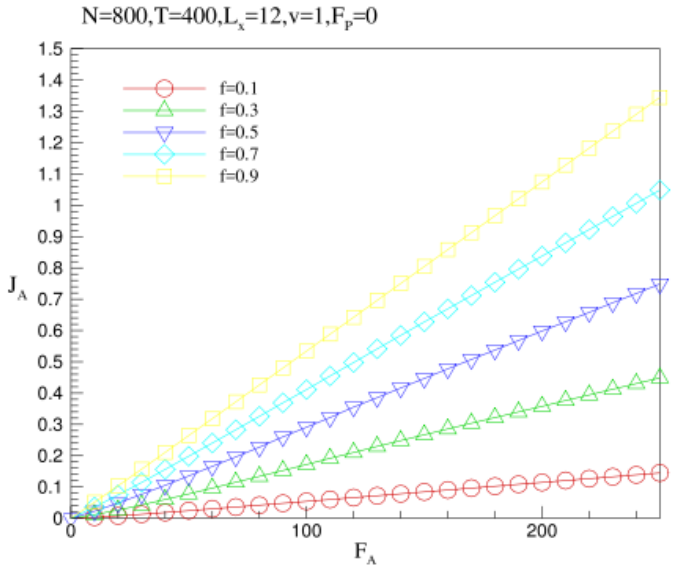

Figure 2: Flow of active particles versus external driving force

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Ion mobility studies in model carbons by solid state MAS- and *In-Situ*-NMR spectroscopy

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Electrical Double Layer Capacitors (EDLC, also denoted as supercapacitors) are important energy storage devices, especially to rapidly store or deliver high amounts of electrical charge. Their energy storage principle is based on the formation of electrical double-layers and depends strongly on the electrode surface as well as other parameters.[1,2] The understanding of the molecular processes in EDLCs are crucial for better design. In the present contribution, we investigate the ion mobility in carbon electrode materials loaded with electrolyte solutions by solid-state NMR spectroscopy.

Well-defined carbon materials of known porosity such as the purely microporous carbide-derived carbon TiC-CDC1000, mesoporous carbon CMK-3 and micro/mesoporous carbide-derived carbon OM-CDC are used in our model studies. These samples were chosen in order to elucidate the influence of the different pores upon the mobility of the electrolyte constitutes. The samples are loaded with well-defined amounts of 1M tetraethylammonium tetrafluoroborate ($TEABF_4$) in deuterated acetonitrile. Solid-state NMR-Spectroscopy is capable of studying host-guest interactions in these electrolyte-loaded carbon materials. ^{11}B, ^{1}H and ^{2}H MAS NMR spectroscopy allows to discriminate between the different electrolyte constituents. Line shape analysis of 1D spectra and 2D EXSY NMR spectroscopy allow to derive the characteristic time scale for processes such as the intra-particle exchange between different pores inside the carbon particle, the exchange between the pore system and the surrounding bulk, and the inter-particle exchange.

In addition to the MAS NMR experiments, the model carbons were also processed into supercapacitors and studied by *in situ* ^{11}B NMR spectroscopy in analogy to experiments performed on commercial supercapacitors by the Grey group[4] and compared with the results of cyclovoltammetric measurements obtained on the same samples. In summary, it could be shown that the presence of well interconnected micro- and mesopores as found in OM-CDC results in a high mobility of the electrolyte ions combined with a very high internal surface area, i.e., high capacitance. The ion high mobility is favorably influences the behavior of the supercap in rapid charge/discharge cycles.

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Mass diffusivities of binary mixtures of normal alcanes with dissolved gases

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Knowledge on the mutual diffusivities of gases dissolved in liquids is of increasing interest for the optimization of processes such as the Fischer-Tropsch synthesis of high valued petroleum products from synthesis gas or the separation of flue gas components. Here, mass transfer is often the rate limiting step compared to, e.g., chemical reactions and/or heat transfer. In a related research project, the benefits of experimental and modelling methods are combined to get a better understanding on how molecular diffusion is affected by the characteristics of the mixture components, which contributes to the development of reliable predictions.

In the present contribution, dynamic light scattering (DLS) experiments and molecular dynamics (MD) simulations were performed at macroscopic thermodynamic equilibrium for a first set of model systems based on liquid normal alkanes and dissolved gases. The solvents *n*-hexane and *n*-decane in their binary mixtures with the solutes hydrogen, helium, nitrogen, and carbon monoxide were studied over a broad temperature range from (298 to 423) K at gas mole fractions below 5%. With DLS, the relaxation behavior of microscopic fluctuations in the properties of state is analyzed. In the case of concentration fluctuations in binary mixtures, their mean decay time is related to the mutual diffusivity which can be accessed by DLS in an absolute way without calibration. The present measurements document that even for small gas concentrations implying weak light scattering signals, reliable mutual diffusivities with typical uncertainties below 5% ($k = 2$) can be obtained. These results serve as a database for MD simulations. Here, thermophysical properties are computed by investigating the dynamics of molecules interacting with each other. Based on suitable models for the mixture components, the self-diffusion coefficient of the gas was determined with uncertainties of about 10% ($k = 2$).

In agreement with theory, similar values for the mutual diffusivity and the self-diffusivity were found. Furthermore, no detectable influence of the solute concentration on the mass diffusivities could be found by DLS and MD simulations within the narrow investigated mole fraction range between about (1 and 5)%. The broad range of mass diffusivities of the studied gas-liquid systems covering about two orders of magnitude from about (10^{-9} to 10^{-7}) $m^2 \cdot s^{-1}$ allow for developing structure-property relationships. Here, effects of the molecular weight and polarity of the various gases as well as the varying alkyl chain length of the solvents on the mass diffusivities are discussed. To further develop the intended prediction scheme, two additional classes of alkane-based solvents featuring the hydroxyl group – namely normal alcohols – as well as bulky charged structures in the form of ionic liquids will be studied in their binary mixtures with the aforementioned gases in a next step. In the same context, the DLS data will be used to test how reliably mutual diffusivities can be computed in MD simulations for the various fluid systems by different approaches.

Immersion enthalpies and adsorption isotherms of liquids on carbon molecular sieves

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Liquid-phase adsorption equilibria [1, 2] are of great interest for designing energy-saving processes in industrial applications such as separation and purification. How fast the adsorption equilibrium state is reached, strongly depends on bulk diffusion effects and the adsorption kinetics of gas or liquid molecules in the pore structures of solids.

In this work, liquid immersion enthalpies and vapor adsorption isotherms of different adsorptives on series of carbon molecular sieves (CMS), called Carboxen materials, are presented. The CMS are mainly microporous with high specific BET surfaces, but they exhibit also a significant mesoporosity in order to ensure a fast kinetics to the adsorption centers in micropores.

The chosen adsorbent-adsorptive systems are going to be model systems for a new experimental device for the adsorption of binary liquid mixtures on porous and/or disperse solids. Whereas binary liquid adsorption isotherms are commonly measured by the batch method [3, 4] allowing no adsorption kinetics, the adsorption device with in-situ analytics allows measurements of the time for reaching adsorption equilibrium. The measured immersion enthalpies of pure liquids on CMS serve to give an insight into interactions at solid/liquid interfaces.

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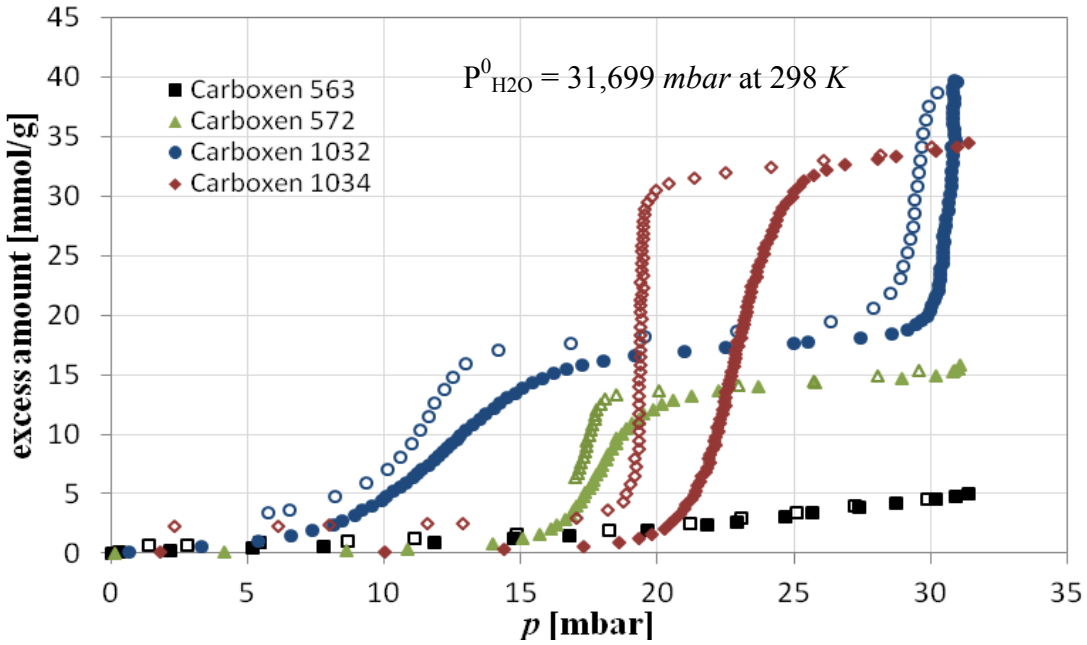

Figure 19: Vapor adsorption isotherms of water at 298 K on four different CMS; Adsorption: filled symbols, Desorption: empty symbols

Transport diffusion of CO_2 in mixed matrix membranes

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Over the last few decades there have been significant research efforts aimed at developing energy-efficient Mixed Matrix Membranes (MMMs) which have great potential for gas separation processes by overcoming the limitation of pure polymeric membranes, namely, the trade-off between permeability and selectivity. Considering the progress on MMM fabrication techniques and enhanced characteristics of new MMM generations, however, there have been relatively few studies carried out on understanding fundamental diffusion phenomena in MMMs. In other words, it is hardly understood how differently the guest molecules, such as CO_2, H_2 and methane, penetrate the two distinctive spaces, i.e. polymer and filler regions, within the MMMs.

With Infrared microscopy (IRM) [1], we have recently investigated the diffusion mechanism of CO_2 molecules in pure 6FDA-DAM polymer sheet. By varying the thickness of the polymer from 25 μ m to 320 μ m, it was found that the diffusional time constant, τ, was linearly proportional to the thickness of the polymer, as shown in Fig. 1. This linear relationship, in turn, means that the CO_2 adsorption in the polymer is strongly limited by the surface barrier instead of the diffusion inside, according the Eq. (1):

$$\tau = \tau_{barrier} + \tau_{diffusion} = \frac{L}{\alpha} + \frac{L^2}{3D_T} \qquad (1)$$

where, $2L$ is thickness, α is surface permeability, and D_T is transport diffusivity. Further research is required to elucidate whether the insertion of fillers alters the limiting step of the CO_2 uptake process in MMMs.

In addition, our IR microimaging technique enabled us to record CO_2 concentration profiles over a MMM consisting of 6FDA-DAM polymer and big ZIF-8 crystals (>70 μm size) during transient adsorption. From this we can directly observe how fast and how much the guest molecules diffusion into and adsorb on to the two different regions in the MMM.

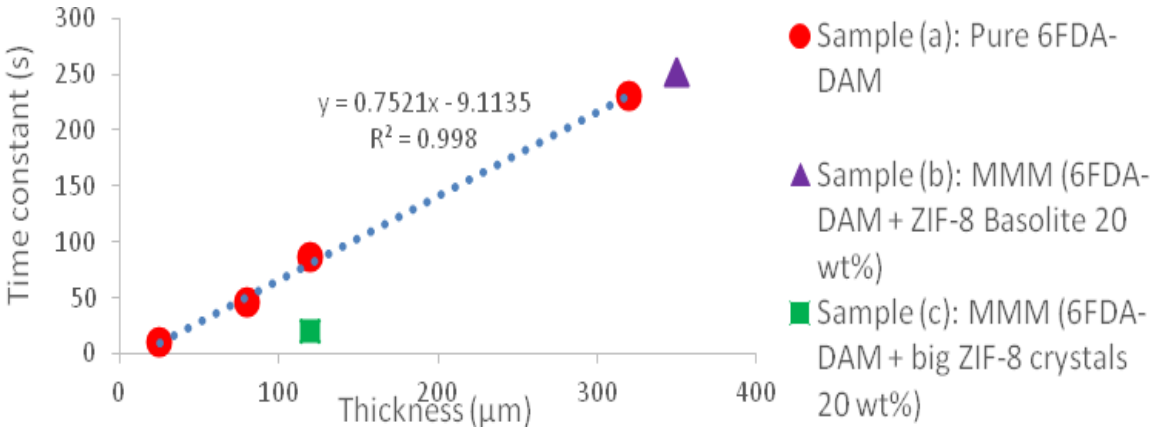

Figure 20: Relationship between diffusional time constant and thickness of polymer

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Pecularities of diffusion in Cu-Fe and Co–Cu alloys

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Interest to the diffusion processes in Fe-Cu and Co-Cu systems is provoked by the recent results: absence of advanced grain-boundary diffusion (GBD) [1,2]. The comparison of the diffusion profiles obtained by electron probe microanalysis (EPMA) method near grain boundaries and far from them (in the grain bulk) are the same. In order to avoid the additional material transport associated with cutting and polishing, which can affect on concentration profile the study on specially prepared foils is suggested. For such diffusion study the additional preparation of samples after diffusion annealing is not required. Experiments were performed on copper foils of thickness about 18 μm. Before the diffusion annealing the grain boundaries were visualized by pre-annealing at high temperature due to Mullins' grooving. The diffusant layer (Ni, Fe or Co) was deposited electrolytically. The accumulation of the diffusing element on the opposite side during the diffusion annealing were measured. It was shown that nickel penetrates and on the grain boundary and through the bulk, but the nickel concentration near the grain boundaries is always higher than far from the boundaries

For samples with cobalt and iron the concentrations of these elements on the opposite side were the same in the grain boundary and the bulk for all regimes of annealing.

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Diffusion-barrier properties and thermal stability of TiAlSiCN, TiAlSiCN/SiBCN, and TiAlSiCN/AlOx films

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The Ti-Al-N protective coatings are widely used in practice (metal cutting and forming tools, roller bearings and other machine parts) because of their high mechanical and tribological properties, good thermal stability and excellent oxidation resistance. The Si incorporation into the Ti-Al-N coating resulted in the formation of nanocomposite structure with the (Ti,Al)N crystallites embedded in the amorphous SiN_x matrix. Nanocomposite structure of the Ti-Al-Si-N coatings promoted to the increasing of the hardness and maximal usage temperature. C-doped Ti-Al-N coatings are characterized by improved tribological properties due to the solid lubricant effect of the amorphous carbon. Recently developed Ti-Al-Si-C-N coating on Al_2O_3 model substrate show high thermal stability of structure and extremely high hardness ~40 GPa up to 1300°C. But for the practical application it's very important to have the high diffusion barrier properties of coatings. The aim of the present work is to investigate the diffusion barrier properties, thermal stability, and oxidation resistance of the Ti-Al-Si-C-N base coatings as well as multilayer (ML) TiAlSiCN/SiBCN and TiAlSiCN/AlOx coatings with additional layers which improve listed characteristics.

TiAlSiCN coatings were deposited using magnetron sputtering of composite targets produced by self-propagating high-temperature synthesis. ML coatings were manufactured by step-by-step magnetron sputtering (TiAlSiCN layer) and ion sputtering (SiBCN or AlOx layers). NiCrAlW disks and alumina plates were used as the substrates. To reveal the diffusion barrier properties and oxidation resistance the as-deposited coatings were subjected to the air annealing at temperatures from 800 to 1000°C. Additional thermo-cycling experiments for 20, 50, and 100 cycles (20-1000°C) were fulfilled. Thermal stability of coatings was estimated by vacuum annealing. The structure, chemical and phase composition of as-deposited and thermal-treated coatings were studied by means of glow discharge

optical emission spectroscopy, X-ray diffraction, transmission and scanning electron microscopy. The coatings were characterised in terms of their hardness, elastic modulus, and elastic recovery.

Results obtained show that in the ML coatings the SiBCN and AlOx layers play role of the barriers against Ni diffusion from the substrate into the coating and thus significantly improve the thermal stability of whole ML coating. TiAlSiCN/SiBCN and TiAlSiCN/AlOx coatings on Al_2O_3 substrates also demonstrate better oxidation resistance (critical temperature of 1100°C) and thermal stability (1400°C) than basic TiAlSiCN coating. Combination of high diffusion barrier properties, high oxidation resistance and mechanical properties makes TiAlSiCN/SiBCN and TiAlSiCN/AlOx coatings promising candidates for protective purposes to be used in different high-temperature applications.

Grain boundary wetting in the Al–Zn and Al–Mg alloys

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In this work the differential scanning calorimetry (DSC) investigation of grain boundary (GB) wetting phase transition in the Al–Zn and Al–Mg alloys before and after high pressure torsion (HPT) has been studied. In Fig.1 and 2 DSC curves for both as-cast coarse-grained and fine-grained HPT-samples for investigated alloys are shown. The shape of melting curves is asymmetric (they have "shoulders"). It was supposed that this two-stage melting is due to the transition from incomplete to complete wetting of GBs by the melt.

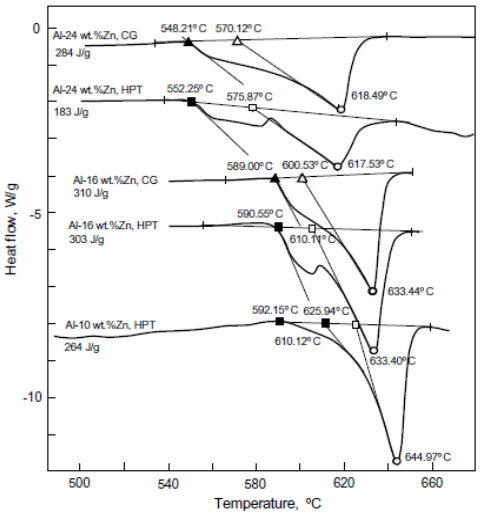

Figure 1: Temperature dependence of heat flow (DSC curves) for the Al–Zn samples. ○ – liquidus temperature, Δ – bulk solidus for coarse-grained alloys, □ – bulk solidus for fine-grained (HPT) alloys, ▲ – GB solidus for coarse-grained alloys, ■ – GB solidus for fine-grained (HPT) alloys.

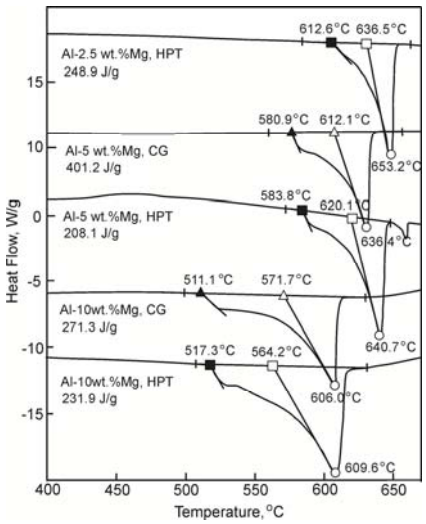

Figure 2: Temperature dependence of heat flow (DSC curves) for the Al–Mg samples: ○ – liquidus temperature; ▲– incomplete wetting of GB for coarse-grained alloys; ■ – incomplete wetting of GB for fine-grained (HPT) alloys; Δ – complete wetting of GB for coarse-grained alloys; □ – complete wetting of GB for fine-grained (HPT) alloys.

In Al–Zn alloys after HPT we observed that the melting starts ~10–25 °C below the bulk solidus line. It means that between GB solidus (premelting) line and bulk solidus the GB contains the layer of a liquid-like phase. Such layers could ensure the extremely high superplasticity of Al-based alloys just below the bulk solidus line [1]. In the contrast to the Al–Zn alloys, the GB solidus line for Al–Mg alloys after HPT is very close to the bulk solidus. The difference between them does not exceed 2 °C. It means that, most probably, the addition of magnesium to the Al-based alloys makes the area between GB and bulk solidus narrower.

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The complete and incomplete grain boundary wetting in the Cu–Co alloys

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The phase transformations in the peritectic system Cu–Co has been studied. Grain boundary phase transformations can significantly change the properties of polycrystals [1, 2]. The most important grain boundary phase transformation is the transition from incomplete grain boundary wetting by the second phase to the complete one.

In this work the Cu–2.2 wt.% Co and Cu–4.9 wt.% Co as-cast alloys was studied. Previously, it was found that if the second wetting phase is solid, rather than liquid, the fraction of wetted boundaries can increase with decreasing, rather than increasing temperature like in systems Al–Zn and Co–Cu [3, 4]. Accordingly, the contact angle decreases with decreasing, rather than increasing temperature. This is because the energy of interphase boundaries (if the second phase is solid) can decrease with increasing temperature more slowly, than the grain boundary energy. It was a priori unclear whether a similar phenomenon will be observed in the case where we deal with a liquid wetting phase which is not enriched, but is depleted by the second component. We saw that in the case of copper–cobalt alloys, this is not observed, and the fraction of completely wetted boundaries and the contact angle behave similarly as for the melt enriched by the second component.

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Study using acoustic waves state of metal alloys after diffusion influences with the aim of predicting their behavior

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Metallic materials commonly used in practical applications objects. Their state plays a leading role in the process of operation. On the condition of the materials is influenced by various external influences. Such influences manifested in the process of manufacture and in the operation should be attributed primarily to processes of diffusion. They substantially change the physical parameters of the surface layers. Therefore, the actual task of assessment of health products and predicting their behavior. For solving this task was proposed to monitor the status of materials by means of acoustic waves (AW), i.e., to use AMD-methods [1,2]. GHz- range was chosen to ensure a sufficiently high resolution.

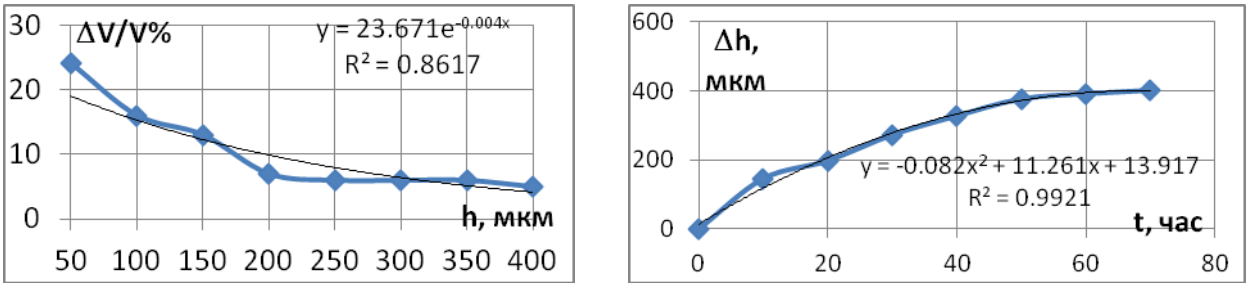

Fig. 1. *a*) the dependence of the absorption level of AW in the surface layers of steel (38XMIOA) depth of nitriding layer (t^0 process 560^0C); *b*) the dependence of the thickness of the layer with altered properties from the time of nitriding (at $t^0 = 500^0$C) obtained by the change of speed υ_R of surface acoustic waves in steel (40XHMA).

The essence of the work was to develop methods for studying the state of the materials and in the assessment of the level of exposure of diffusion processes using the AMD methods. The objects of the study - model materials, and steel of various types. It is experimentally shown that AMD-methods sensitive to diffusion effects. For example, the processes of carburizing and nitriding of steels demonstrates the dependence of the number of characteristics of acoustic waves (AW) from the parameters of diffusion processes. These settings include, first, the concentration of a substance- diffusion, temperature and time of process. In Fig.1 shows examples of the dependence of the absorption level of AW in the

surface layers of steel from the depth of the nitriding layer and the dependence of the thickness of the layer with altered properties from the time of nitriding obtained by the change of speed υ_R of surface acoustic waves in steel .

The experiments confirm the high sensitivity of AMD-methods as parameters of the diffusion processes and their changes [3]. This fact allows to monitor the processes of diffusion, to control the structure of materials, identify and characterize system defects (e.g., microcracks, pitting, etc.).

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The determination of the physical parameters of the subsurface layers of solid materials using AMD-methods

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Currently one of the most urgent material problems is the problem of studying the structure and properties of solid materials non-destructive way, the definition of the boundaries of their applicability. In the end, the structure determines the condition of the material actually given by a superposition of the physical parameters of the selected volume. Changing these values allows judging the state of the surface layers of solid materials. Effective methods control the state of these layers are AMD-methods [1,2].

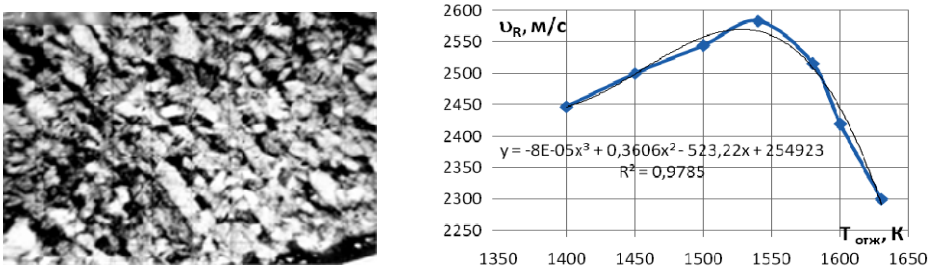

Fig. 1. a) Acoustic image of the grain structure (steel, scale 100-150 μm, Z = -14 μm); b) Dependence υ_R from $T_{ann.}$ piezo-ceramic (PZT-22) received AMD-method.

The essence of the work was to develop methods for studying the state of the materials and in the assessment of the level of exposure of diffusion processes. Objects of study – ceramic materials and steels of various types.

In the mode of acoustic imaging has got the image of the grain structure of the steel (Fig.1*a*) and grain size was calculated strength characteristics. After the diffusion treatment was varied grain structure, and hence the values of the parameters of the material. To ensure the objectivity and reliability of the measurements experiments were carried out on model objects with known characteristics-sticks (single crystals, glass, pure metals). Developed and applied a method of calculating parameters of the samples by the values of speed and attenuation coefficients of surface acoustic waves (saw) [3]. It is possible to obtain study materials for the correlation of velocities of surfactants on the parameters of the effect on the material (temperature, time). In Fig.1*b* shows one such dependency of the piezo-ceramics.

The obtained results demonstrate the effectiveness of the use of AMD-methods for the determination of the physical parameters of the surface layers of solid materials and ensure their accuracy.

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Application of frequency response methods for measuring heat and mass transfer in sorption materials for heat transformation

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Periodically operated heat transformers use the difference in vapor pressure of the pure refrigerant (here water) and the refrigerant bound to a sorption material. They allow the construction of efficient thermally driven heat pumps, chillers or compact heat storages [1]. The principal component of such equipment is the sorption heat exchanger (SHX) which is in contact with the sorption material on one side. It is operated alternatingly between sorption and desorption of the refrigerant at low pressure/low temperature and at high pressure/high temperature respectively. The SHX acts as thermally driven compressor. In combination with an evaporator and a condenser, heat pumps and chillers are realized. Next to conventional sorption materials like zeolites and silica gels, hygroscopic salts have a high potential for the use in SHX [2, 3].

Mass transfer (mostly diffusion) of the refrigerant and the transfer of heat of sorption in the SHX are important transport mechanisms that often limit the overall performance. Design and optimization depend on a thorough understanding of these mechanisms. Challenges are their typically non-linear nature and the strong coupling between heat and mass transfer.

One approach to identify the transport coefficients is the volume swing frequency response (FR) method [4]. The experiment depicted in Figure 21 has been set up. A sample of sorption material (e.g. a cutout from a SHX) is placed in a small measuring chamber with a pure refrigerant atmosphere. After a preconditioning phase, the chamber volume is excited

sinusoidally so that the pressure and sample surface temperature response with sinusoidal signals. The amplitude ratios and phase shifts between excitation and response are measured for different frequencies. By comparison to a heat and mass transfer model the transport coefficients (e.g. diffusion coefficients) can be identified.

First FR measurements were conducted on zeolite Y samples with water as refrigerant. Results are presented and compared to results from pressure jump and temperature jump experiments [5].

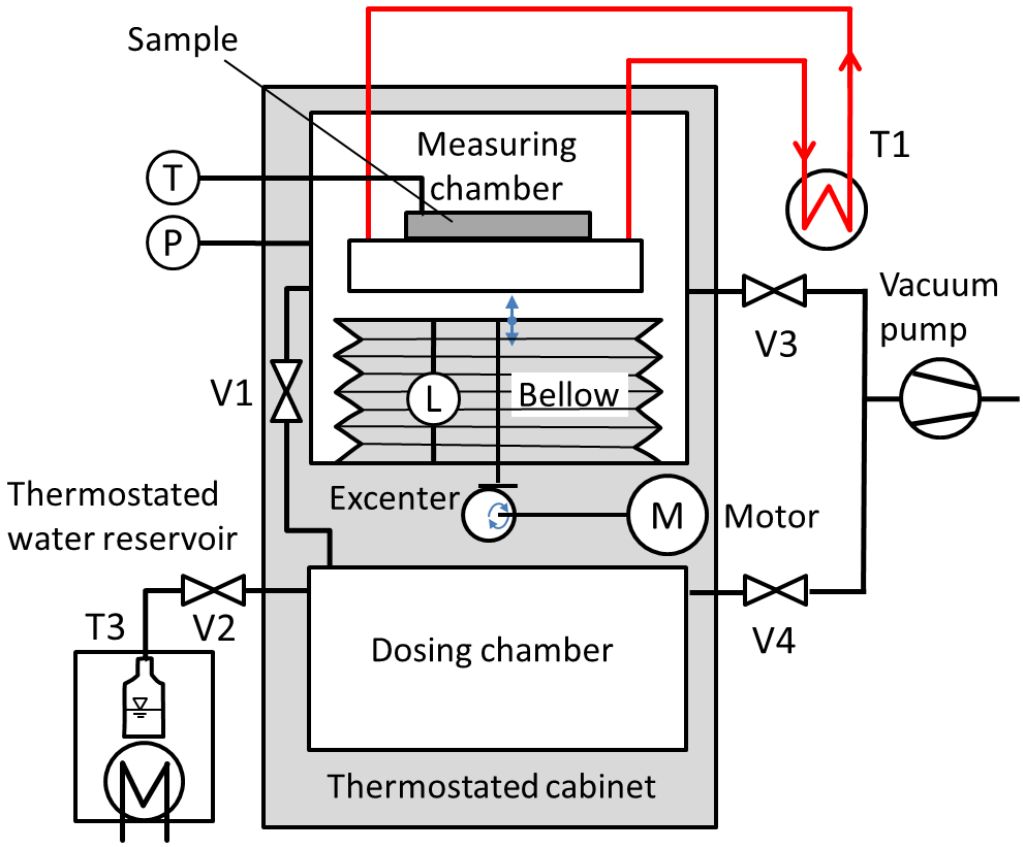

Figure 21: Schematic of the new volume swing frequency response apparatus

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The dependencies of self-diffusion coefficient on the size and shape of the nanocrystal at different *P*-*T*-conditions

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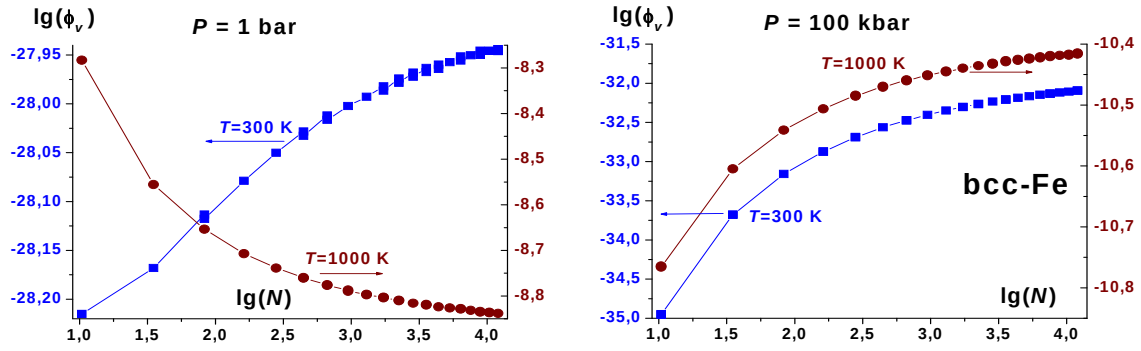
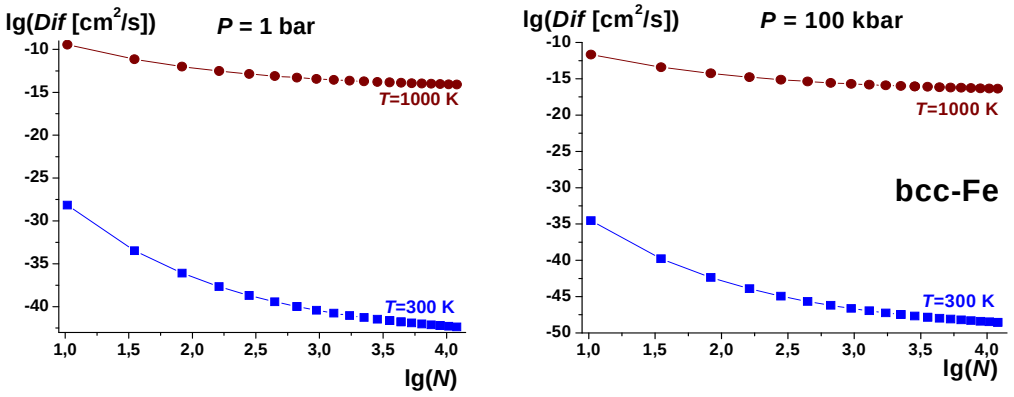
The previously proposed RP-model [1, 2] was generalized to the case of the vacancies and the delocalized (i.e. diffusing) atoms presence, which are uniformly distributed throughout the volume of the simple matter nanocrystal with *N*-atoms. On the basis of the generalized RP-model, the vacancy formation probability (ϕ_v) and the atom delocalization probability (x_d) dependencies on the size and shape of BCC-iron nanocrystal at different *P*-*T*-conditions were studied.



It is shown that when an isothermal pressure increases, the function $\phi_v(P)$ decreases more significantly for nanocrystal than for bulk crystal, and at a certain pressure, the probability of vacancy formation in nanocrystal becomes smaller than in bulk crystal. At the isobaric-isothermal nanocrystal growth under atmospheric pressure and temperature 300 K, the nanocrystal contains fewer vacancies per atom than the bulk crystal. However, at 1 bar and 1000 K, the size reduction of crystal leads to higher probability of vacancy formation (Fig. 1, left). At nanocrystal formation under P = 100 kbar the nanocrystal contains fewer vacancies per atom than the bulk crystal both at 300 K and at 1000 K (Fig. 1, right).



At nanocrystal size reduction the probability of the atom delocalization (x_d) and the self-diffusion coefficient ($Dif \sim x_d$) are increasing at any pressure and temperature (Fig. 2).

At the nanocrystal shape deviation from the most optimal shape (for RP-model – from the cubic shape), the size dependences of the activation parameters for the nanocrystal are increasing.

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On the liquid-like local state in deformed metallic materials, relevance to physics of the diffusion and other anomalies

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On the basis of results [1-8] of thermodynamic analysis of a number of experimental data, the process of periodical formation of the liquid-like state in nanoregions of the extremely "non-equilibrium" grain boundaries ($ГЗ_3$; Figs. 1, 2) and in other defect regions in metallic materials under the superplastic deformation and under the intensive plastic deformation is considered. The liquid-like state is characterized by an anomalously high diffusion coefficient ($D^*_{ГЗ3}$, as in a liquid phase) and anomalously low shear modulus (in comparison with the glass-like amorphous structure). The physics of its influence on processes, including the diffusion ones, and materials properties is also considered.

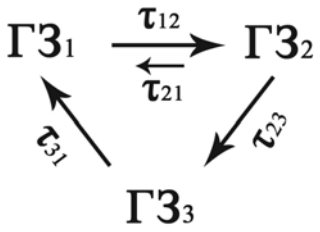

Fig. 22: Three extreme states of grain boundaries (ГЗ)

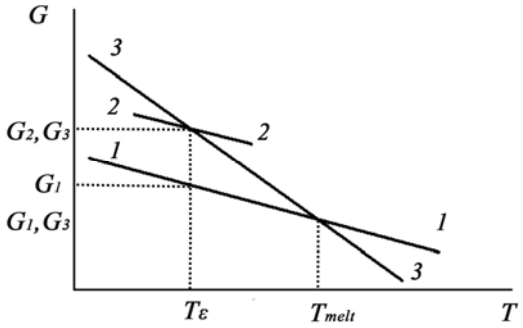

Fig. 2: Temperature dependence of the free energies (G)

According to data [9], the superplasticity deformation rate ($\dot{\varepsilon}$) for Zn–22%Al alloy is described as:

$$\dot{\varepsilon} = A(D^*_{ГЗ}G^*b/kT)\,(b/d)^p\,(\sigma/G^*)^n, \qquad (1)$$

where $\dot{\varepsilon} = 0.01\ s^{-1}$; A = 15; $G^* = 40$ GPa; $b = 0.28$ nm; $T = 503$ K; $d = 2.5$ μ; p = 2; σ = 8 MPa; n = 2.

Hence, $D^*_{ГЗ} = 8\cdot10^{-6}\ sm^2s^{-1}$; the obtained diffusion quantity (as $D^*_{ГЗ3}$) is typical for a liquid phase.

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The compound-like nanosegregation at dislocations and grain boundaries in metallic materials, relevance to physics of the diffusion anomalies

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According to [1-9], **the apparent diffusion coefficient of an impurity (D_Σ)** in metallic systems with dislocations (⊥s) or grain boundaries (GBs), **<u>for the regime A,</u>** can be described as:

$$D_\Sigma = [D\cdot(1- \eta_{\perp GB}) + D_{\perp GB}\cdot\eta_{\perp GB}(\partial C_{\perp GB}/\partial C)] / [1 - \eta_{\perp GB} + \eta_{\perp GB}\cdot(\partial C_{\perp GB}/\partial C)], \quad (1)$$

$$C_\Sigma \approx C\cdot(1-\eta_{\perp GB}+\eta_{\perp GB}\cdot K_{\perp GB}), \quad K_{\perp GB} \approx (\partial C_{\perp GB}/\partial C) \approx (C_{\perp GB}/C) \approx exp(\Delta S_B/R)\cdot exp(-\Delta H_B/RT), \quad (2, 3)$$

$$\boldsymbol{D_{\perp GB} \approx (D_\Sigma\cdot C_\Sigma - D\cdot C) / (C_\Sigma - C),} \quad (4)$$

where ΔH_B (< 0) is the bonding energy with ⊥s or GBs; $D_{\perp GB}$ is the diffusion coefficient in ⊥s or GBs.

If $(\eta_{\perp GB}\cdot K_{\perp GB}) \ll 1$, then $\boldsymbol{D_\Sigma \approx [D + D_{\perp GB}\cdot\eta_{\perp GB}\cdot K_{\perp GB}]}$ – the Hart-Mortlock type equation ($\boldsymbol{D_\Sigma > D}$); it is the case of the Cottrell type nanosegregation, which can be "easy diffusion paths".

If $(\eta_{\perp GB}\cdot K_{\perp GB}) \gg 1$, then $\boldsymbol{D_\Sigma \approx [D_{\perp GB} + (D/\eta_{\perp GB}\cdot K_{\perp GB})]}$ – the modified Oriani type equation ($\boldsymbol{D_\Sigma < D}$); it is the case of the non-Cottrell (compound-like) nanosegregation, it can be non-easy diffusion paths.

Some systems and diffusion processes are in detail considered [1-9], including the following ones: (1) the hydride-like nanosegregation of hydrogen at dislocations and grain boundaries in palladium and their influence on the apparent characteristics of hydrogen solubility and diffusivity in palladium; (2) the physics of the anomalous characteristics of diffusion of Fe and other transition impurities in crystalline Al at elevated temperatures, the role of the compound-like nanosegregation (CLNS) of Fe

and the others at dislocations and grain boundaries in Al, analysis of the Mössbauer and diffusion data on CLNS of Fe at grain boundaries and dislocations in Al; (3) some new physical aspects of internal oxidation and nitridation of metals (for Cu-0.3% Fe alloy/Cu_2O surface layer, and for (Ni-5% Cr) alloy / N_2 gas), the role of CLNS at dislocations and grain boundaries, study results on the large deviations from the classical theories predictions and their interpretation.

The possibility is considered of nanotechnology applications of the study results for creation of nanostructured metals with CLNS structures at grain boundaries, in order to obtain specific physical and mechanical properties of such cellural-type nanocomposites. In particular, it can be created complex hydride-like, carbide-like, carbohidride-like, nitride-like, carbonitride-like, boride-like, oxide-like or intermetallide-like nanosegregation structures at grain boundaries in such materials.

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Atomic mechanisms and characteristics of diffusion, sorption and intercalation of hydrogen in nanographite and graphene structures

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On the basis of results [1-10] of thermodynamic analysis of a number of the most cited experimental and theoretical data, the atomic mechanisms and characteristics of diffusion (Eqns. 1, 2), sorption (including some chemisorption (Fig. 1)) and intercalation of hydrogen in nanographite and graphene structures are considered.

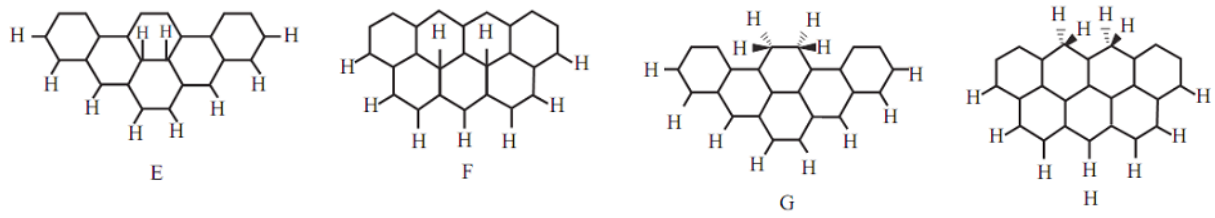

Fig. 23: Some theoretical models of chemisorption of atomic hydrogen on the basal and edge planes of graphite: "F" – process III (ΔH_{III} = -2.5 eV); "H" – process IV (ΔH_{IV} = -3.7 eV).

According [1-4], the apparent diffusion coefficient ($D_{III,IV}$) and the apparent activation energy ($Q_{III,IV}$) of diffusion of hydrogen atoms in nanographite and graphene structures are described as:

$$D_{III,IV} \sim (D / K_{III,IV}) \, , \, Q_{III,IV} = (Q - \Delta H_{III,IV}) \approx -\Delta H_{III,IV}, \qquad (1, 2)$$

where D and Q (≈ 0.1 eV) are the quantities for the case without the chemisorption ifluence, $K_{III,IV}$ are the related equilibrium constants, $\Delta H_{III,IV}$ are the chemisorption energies.

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Effect of local chemical composition of grain boundaries on corrosive resistance and mechanical properties of ultrafine-grained titanium alloys

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Industrial alloy PT3V composed of Ti-4.73wt.%Al-1.88wt.%V formed the target of this research. The ultrafine-grained (UFG) structure in the alloy was obtained through equal channel angular pressing (ECAP) at the temperature of 723-743 K.

In its initial state (before ECAP) the alloy structure is characterized by heterogeneous distribution of grains by size from 10-20 μm to 100 μm. The analysis of diffraction patterns obtained from some grains of a coarse-grained alloy shows that these are α-Ti grains. The energy-dispersive analysis reveals two types of grain boundaries (GB) in the structure of coarse-grained alloys. First, there are 'clean' GB that form an absolute majority in the alloy structure. The aluminum concentration in such GB is 3.8±0.9 wt.%, whereas the average vanadium concentration is 1.9±0.2 wt.%. The aluminum concentration in surrounding GB is 3.6±0.9 wt.%, whereas the vanadium concentration is ~1.4±0.2 wt.%. Second, these are grain boundaries the vanadium concentration in which may reach 10 wt.%. The average aluminum concentration in the titanium lattice close to such GB is ~4 wt.%, whereas the vanadium concentration is ~1.6 wt.%. Such grain boundaries are limited in number.

The average grain size in alloy after N=4 ECAP cycles is 0.2-0.5 μm. Grains are mainly elongated in shape, but there are a lot of equiaxed grains as well. Grain boundaries are clean with no excess vanadium segregations similar to those observed in a coarse-grained alloy. The results of the energy-dispersive analysis show that the spread in aluminum and vanadium concentrations between separate grain boundaries is insignificant.

With the increase in the number of ECAP cycles to N=4 there is an increase in the macroelasticity strength, yield strength and hardness from 420 to 750 MPa, from 620 to 1020-1050

MPa and from 1.9-2.0 to 3.5-3.6 GPa, respectively. Along with high strength, the UFG alloy at room temperature is characterized by high ductility δ_{max}=47.5-50%. Ductility grows from 225 to 475% in the UFG alloy with the deformation temperature growing 873 to 1073 K. In coarse-grained alloys, a similar rise in the deformation temperature leads to ductility growing from 85 to 220%. Fractures in coarse-grained and UFG samples are ductile in nature.

Hot salt corrosion tests performed on alloy in the original state show that the corrosion-affected layer after 500 h of tests at T=523 K is L_{cor}=500-600 μm deep. Corrosion is intercrystallite. Similar tests on the UFG alloy show that the nature of corrosion processes does not change with corrosion propagating primarily along grain boundaries. However, the depth of the corroded layer in the UFG alloy does not exceed L_{cor}~100-150 μm. Thus, the results of the tests prove a significant increase in corrosion resistance of UFG alloys as compared to coarse-grained materials.

It was shown that a simultaneous increase observed in corrosion resistance, strength and ductility may be related to diffusion-controlled atomic rearrangement of alloying elements (aluminum, vanadium) along the GB of a alloy during ECAP. Along with the formation of new GB during ECAP at elevated temperatures, there is a diffusion redistribution of atoms of alloying elements from 'old' GB to 'new' ones. Vanadium with high concentration along the original GB of a coarse-grained alloy balances the concentration and diffuses along the boundaries to 'clean' grain boundaries formed during ECAP. At the same time the local concentration of vanadium atoms along the GB decreases due to a significant increase in the overall area of grain boundaries.

It shall be noted that a decrease in the concentration of alloying elements along the GB of the UFG alloy contributes to 'easier' movement of lattice dislocataions through GB and reduces the defect accumulation rate along the grain boundaries. Consequently, the intensity of junction disclinations leading to microcracks along the GB is drawn down. This increases the ductility of the UFG alloy.

The research was performed with the support of the Russian Science Foundation (Grant 16-13-00066).

Abnormal strengthening effect after annealing of ultrafine-grained metals produced by ECAP

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It is traditionally assumed that the dependence of strength characteristics of submicrocrystalline (SMC) metals on the annealing temperature has three stages: slight changes in strength during annealing below the recrystallization initiation temperature ($T_{ann}<T_1$) due to recovery processes, rapid softening associated with intensive grain growth during heating of SMC metals ($T_1<T_{ann}<T_2$), and slight changes in strength at higher annealing temperatures ($T_{ann}>>T_2$). At the same time, the analysis of published data shows that annealing of some SMC metals causes the abnormal strengthening effect: these metals become stronger while heating to the temperature that corresponds to the recrystallization initiation temperature.

The target of this research is to study the abnormal strengthening effect observed while annealing of SMC metals. To identify mechanical properties (macroelasticity limit σ_o, yield limit σ_y and K ratio in the Hall-Petch equation) microsamples were evaluated using the method of relaxation compression tests.

It was found that the dependence of σ_o and K ratio on the annealing temperature is determined by the nature of recrystallization processes. In case of abnormal grain growth during annealing of SMC metals, the abnormal strengthening effect is observed and a nonmonotonic dependence of K ratio on temperature takes place. In case of common recrystallization, with the increase of the annealing temperature in SMC metals, macroelasticity limit σ_o is gradually falling and K ratio is growing.

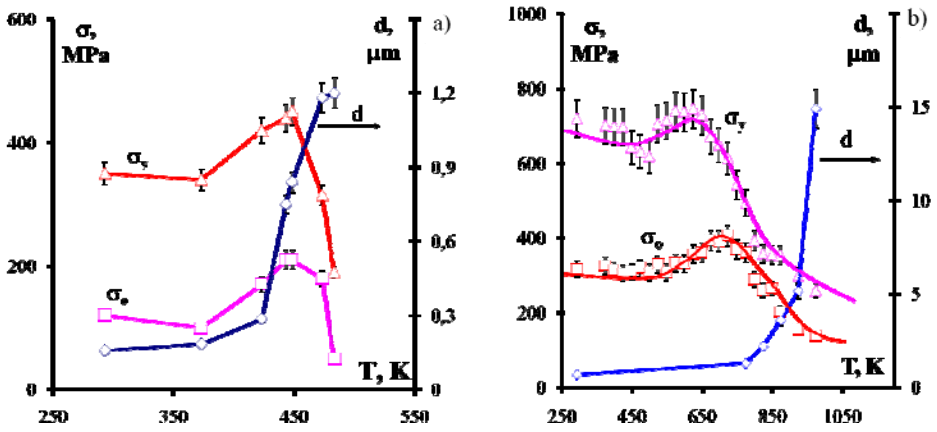

Figure 1: Dependence of $\sigma_o(T)$, $\sigma_y(T)$ and d(t) of SMC copper (a) and SMC titanium (b)

It was shown that the abnormal strengthening effect in SMC metals is rather large-scale: σ_o grows by 50-300% whereas σ_y grows by 10-50% as compared to σ_o and σ_y after ECAP. It was found that the abnormal strengthening effect is observed during annealing at temperatures close to the recrystallization initiation temperature, the scale of increase in macroelasticity limit $\Delta\sigma_o$ far exceeds the scale of changes in yield limit $\Delta\sigma_y$ and microhardness ΔH. Comparative analysis of $\sigma_o(T)$ and $\sigma_y(T)$ dependencies shows that the behavior of dependencies $\sigma_o(T)$ and $\sigma_y(T)$ is uncorrelated, and T_{max} corresponding to maximum strengthening for $\sigma_y(T)$ dependence appears to be shifted to the area of lower annealing temperatures as compared to $\sigma_o(T)$ dependence.

A model was offered for the abnormal strengthening effect that occurs during annealing of SMC metals. The model is based on the ideas underlying the theory of noneqilibrium grain boundaries in metals. It was shown that the abnormal strengthening effect during annealing of SMC metals is related to the accumulation of defects along migrating grain boundaries. Formulae were developed that help to link paramters of the Hall-Petch ratio with the grain boundary migration rate, nonequilibrium level, lattice dislocation density, as well as annealing temerpature and time. Numerical calculations were compared to the experimental results, and their close agreement was proven.

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Effect of mechanical activation on optimal sintering temperature of ultrafine-grained tungsten heavy alloys

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Alloy 95wt.%W-3.5wt.%Ni-1.5wt.%Fe constitutes the target of this research. Alloys were produced using tungsten powder with average particle size of 3.9 μm, nickel powder with average particle size under 20 μm, iron powder with average particle size under 11 μm. Nanopowder compositions were obtained through mechanical activation (MA) in a planetary mill APF-3 with acceleration of grinding bodies equaling 60g (rotation rate $V_{ма}$=1450 rpm, time of mechanical activation $t_{ма}$=20 min). The alloys were sintered using the method of sintering in hydrogen (HS) and Spark Plasma Sintering (SPS).

Research into the structure of 95W-3.5Ni-1.5Fe powder composition after high-energy mechanical activation shows that the average size of tungsten particles does not exceed 100 nm. Analysis of diffraction patterns proves that with the increase in MA time, tailing of X-ray peaks corresponding to α-W is observed. With the increase in MA time, asymmetric tailing of α-W peak (110) is observed towards larger reflection angles. This indicates the formation of a supersaturated solid solution of nickel and iron in the surface layer of α-W particles.

The dependence of density on the temperature of sintering in hydrogen has two stages both for coarse-grained and mechanically activated nanopowders. Optimal sintering temperature T_1 for mechanically activated powders in hydrogen is 1300 °C, which is 150-200 °C less than the optimal tempertaure of sintering in hydrogen for coarse-grained powders (~1450-1500 °C).

Dependences of density on SPS temperature have a similar two-stage nature. The optimal SPS temperature for mechanically activated powders at the heating rate of $V_н$=100 °C/min is T_1~1100 °C. Reduced heating rate leads to a shift in the optimal SPS temperature to higher values: at the heating rate of 50 °C/min the optimal SPS temperature is T_1=1200 °C. Note shall be taken that the optimal SPS temperature for coarse-grained powders is ~1300 °C.

While summarizing the outcome of experimental studies, two major results shall be taken note of: 1) decrease in the optimal sintering temperature for mechanically activated nanopowders and 2) increase in the sintering intensity of nanopowders during flash sintering. The intensity of diffusion mass transfer (I) is proportionate to the diffusion ratio D exponentially dependent on the activation

energy of the diffusion process Q ($D=D_0\exp(-Q/kT)$) and to the diffusant concentration gradient (C): $I \sim -D\cdot\mathrm{grad}C$, where D_0 stands for pre-exponential factor, while k is Boltzmann constant.

It was shown that the reason for a decrease in the optimal sintering temperature of mechanically activated nanopowders is a reduction in the sintering activation energy corresponding to the grain boundary diffusion activation energy. During high-energy MA, the relaxation of stored energy takes place through the formation of grain boundaries in γ-phase particles that have an increased defect concentration. As a result, diffusion permeability of γ-phase grain boundaries after MA appears to be much higher than diffusion permeability of 'ordinary' grain boundaries in γ-phase that form as a result of sintering separate γ-phase particles with each other. Enhanced diffusion permeability found with grain boundaries of deformation origin leads to an increased intensity of tungsten atoms diffusion through γ-phase, and consequently to a decrease in optimal sintering temperature for UFG tungsten alloys.

It was shown that enhanced intensity that characterizes sintering of mechanically activated nanopowders of W-Ni-Fe system during high-speed heating occurs due to changes in the tungsten concentration gradient $\mathrm{grad}(C_w)$ between α-W particles and γ-phase which is a solid solution of iron and tungsten in nickel.

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Magnetoplastic effect in Cu-Be alloys

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Data about magnetoplastic effect (MPE) in metal alloys which arises in alloys after ageing in magnetic fields, are rather limited and controversial. At the same time MPE in metal alloys represents great interest from the point of view of atom-spin micromechanics and practical application in modern manufacture technologies of nanomaterials with guided properties.

For an establishment of mechanisms MPE model Cu-Be-alloys with various contents of Be, Ni and the maintenance of other magnetic impurity less, than 0,05 wt. % have been prepared and experimentally investigated [1]: 1) beryllium bronze BrB-2 (technical alloy); 2) binary alloys Cu-Be (high purity materials, maintenance Be from 0.5, 1.0, 1.6, 2.7 up to 3.0 wt. %) and 3) triple alloys Cu-2 wt. % Be with additives from 0.4 and 1.0 wt. % Ni. In the given work the possible micromechanisms of MPE in metal alloys of Cu-Be type with additives of nickel are discussed. Here MPE acts as the tool of studying of type and properties of obstacles (impurity atoms, spin clusters, nanophase evolution of intermetallic compounds, impurity segregation in interfaces with atomic and magnetic ordering) for moving dislocations. Discussion is spent in view of a new data about grain boundary impurity segregation, thin microstructure, magnetic properties and phase conditions of alloys, aged in magnetic fields.

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A model for language dynamics in Carinthia, Austria

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Language shift is a linguistic phenomenon that occurs when people give up use of one language for another [1]. In these situations, use of the dominant language increases while the minority language is used less and less. This development can be described by physical models which apply the concept of physical diffusion (movement of atoms) to linguistics (movement of languages) in order to track language spread over time and space.

We present a spatio-temporal model based on cellular automata [2] to simulate the spread of languages. In our model [3], the surveyed geographic area is divided into lattice cells. For each cell and time-step, the probability p of speaking a language is proportional to the number of speakers present in the preceding time step as well as to the interaction with other speakers of the same language.

We apply this model to the languages spoken in Carinthia, Austria where use of the minority language Slovenian has been steadily declining while use of the dominant language German increases. Using empirical data from the Austrian census (1880–2001) for calibration, the model allows us to follow the evolution of language use over time and space on a very small scale (cell size 1 km × 1 km). Thus, the model offers a large-scale complement to the traditional sociolinguistic smaller-scale study of language shift.

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Estimation of line tension of individual dislocations from the thermal motion trajectories of inclusions attached to them

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Method for experimental determination of the line tension of individual dislocation fixed at its ends is proposed. The former uses transverse component of the displacements of inclusions attached to it. The displacements are related to random oscillations of the inclusions being exhibition of their thermal motion. The method is realized using *in-situ* TEM for a fixed dislocation segment with nanosized liquid Pb inclusions attached to it in Al-rich alloy.

Formation of intermediate phases and supersaturated solid solution in Al-Cu system during diffusion

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With the use of the methods of optical microscopy, scanning electron microscopy and electron microprobe analysis the studies of diffusion processes in the aluminum - copper system were carried out in the temperature range 320 - 440 °C. Special attention was paid on the state of the system near Al/Cu interface. It was determined that the intermediate phases in the system, corresponding to the equilibrium phase diagram, were not formed at low temperatures. In this case supersaturated solid solution of copper in aluminum could be observed near the interface. Annealing at high temperature leads to the layer-by-layer formation of the equilibrium phases.

Role of boundaries during wetting and diffusion interaction of heterogeneous metals

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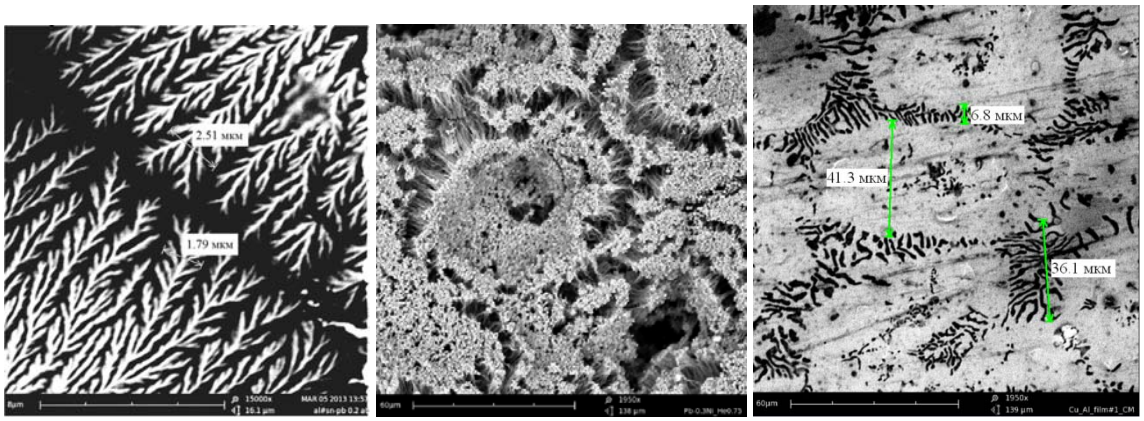
Grains Boundaries in metals render essential agency, both on diffusion interactions of heterogeneous metals, and on processes of wetting by fluid melts of a surface of metal substrates.

So at wetting in vacuum 0.01 Pa an aluminium substrate by stannous at temperature more than 900 K observes a threshold of wetting, small additives of lead to stannous downgrade temperature of a threshold of wetting.

Prior to the beginning of wetting prestress distribution of solder along microscores and boundaries of grains of aluminium is observed. The atoms which are taking place on these boundaries, have an excess energy, therefore at high temperatures probably livelier dissolution of grain boundaries in a melt along which the stannic melt prestressly spreads out. Thus solder dissolves intense sections of boundaries of grains, or enters contact melt with aluminium, and then crystallized as arborescent structures of micrometer gauge (see figure 1*a*).



a *b* *c*

Figure 1. *a* - the Substrate of aluminium wettable with melt Sn-0.6 ат. % Pb, 15000×;
b - Morphology of a surface of nickel sheet NP-2 near to a drop of melt Pb - 0.3 ат. % Ni, 1950×;
c - the Photo of a granular structure on film Cu/Al, 1950×

The analogous effect is observed at wetting by melt Pb-0.3 at. % Ni in vacuum 0.02 Pa surfaces of nickel of brand NP-2.

Studying morphology of a surface of sheet NP-2 after wetting (near to a drop) along boundaries of grains growth of fibrous structures has been observed (see figure 1*b*).

The role of boundaries of grains is manifested at diffusion interaction of heterogeneous films, for example films Cu/Al, which are vapor-deposited on optical glasses of brand C8 which were soaked at temperature 560°C too.

On separate sections of film Cu/Al the structure is consists of grains. Eutectic formations are observed along boundaries of grains (see figure 1*c*). The provisional size of grains is 41.3 microns.

Investigation of time-temperature relationships of surface segregations forming under internal adsorption of solved elements in α-Fe alloys, using Auger-spectroscopy

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Temperature mechanisms of the surface segregations development in α-Fe alloys were experimentally investigated, using Auger-spectroscopy method. It was shown that there are certain temperature intervals of solved elements surface segregations forming in α-Fe alloys during isothermal exposing in vacuum. The temperature scale positions of the solved elements surface segregations in low-carbon steels and ferrous-based alloys found to correlate with the activation energy values of the volume diffusion.

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Grain Boundary Engineering in polycrystalline materials

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The manipulation of microstructure to obtain desires properties is one of the fundamental goals of the field of materials science and engineering. The grain boundary faceting-defaceting transition on facets and roughening transition on grain boundary ridges presents the possibility of modify the grain boundary properties by heat without changing the grain orientations. If a grain boundary is rough, its structure and properties will be nearly isotropic with respect to both the misorientation angle between the grains and the boundary plane. Therefore, if all grain boundaries in a polycrystal are rough, they will have nearly uniform structures and properties. The specimens that will be quenched from high temperatures will show that the rough boundary structures can be largely retained during cooling without developing kinked structures. On the other hand, if the heat-treatment temperatures below the roughening or faceting transition temperatures of most of the boundaries, the grain boundaries will develop flat segments and ridges to produce singular structures. It is thus possible to produce either quenched rough or singular grain boundaries by simply heat-treating the grain boundaries at temperatures above or below phase transition temperature for most of the grain boundaries. The grain boundary faceting-defaceting and roughening transition may have important implications for obtaining the grain boundaries with desired structures and properties.

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International scientific cooperation as a mechanism for diffusion of competences in the field of advanced manufacturing technologies

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Two main channels of technology diffusion can be identified: innovation spillover and innovation transfer, which includes license trading, global innovation activity of multinational corporations and global S&T cooperation. We concentrate on the last one, considering S&T collaboration in the sphere of advanced manufacturing technologies (including robotics, additives, M2M, biotechnology).

Strategy of international S&T collaboration is decisive for participating organizations (obtaining competences) and its influence on the technology level of the location (as a result of technology transfer, staff migration etc.). Collaboration with organizations-leaders in particular field means not only getting competences, but also may have a number of significant shortcomings: necessity for attraction of additional resources to motivate foreign partner and for creating the system of competences reproduction. The most promising option is the collaboration in terms of relative leadership in specific areas (for instance, high level of publication activity in different topics in the same sphere) - it implies the mutual interest in the emergence and development of cooperation.

So the development of model of acting and potential international scientific collaborations identification and assessment is considered to be an important research task. Our model is based on complex analysis of competences and includes 18 indicators, which can be grouped into four blocks: scientific publication analysis, patent landscapes, research grants analysis, participation in industrial clusters. For example, Russian organization compares two potential collaborators in the field of autonomous systems. Figure 1 shows that TU Ilmenau has highly cited articles and experience in collaboration with Russian institutions, while South China University of Technology is active in publishing articles and in patenting, so the choice of academic partner depends on purposes of Russian organization.

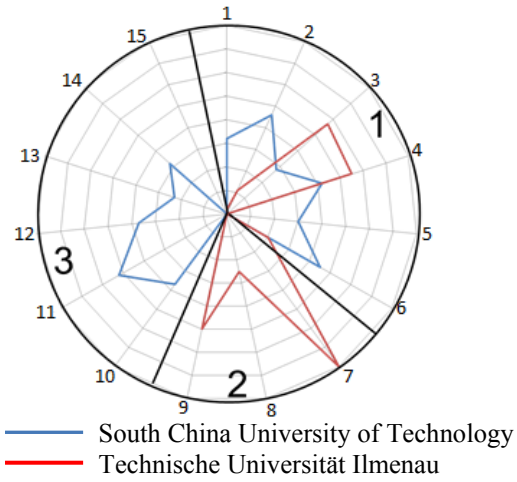

Figure 1: Comparison between potential partners (topic: autonomous systems, sphere: robotics), indicators are normalized to the maximum

Publications	1. Number of articles in topic 2. Number of articles in sphere 3. Field-Weighted Citation Impact in topic 4.Field-Weighted Citation Impact in sphere 5.Number of articles in collaboration in topic 6. Number of articles in collaboration in sphere
Experience in collaboration with Russia	7. Number of articles in collaboration with Russia in topic 8. Number of articles in collaboration with Russia in sphere 9. Number of articles in collaboration with selected Russian university in topic
Patents	10. Number of patents in topic 11. Number of patents in sphere 12. Number of citation patents in topic 13. Number of citation patents in sphere 14. Number of active patents in topic 15. Number of active patents in sphere

This model enables for a comparative analysis between the various alternatives under consideration. Such a comparison is necessary, due to the large heterogeneity of the included indicators and the various purposes that organizations can set themselves while finding potential foreign partners. In some cases, an organization may be interested in joint research, in others - in the commercialization of its competencies, or in applied works. In each case, the importance of indicators will be different.

X-rays diffuse scattering by water and amorphous ices

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Water is a unique natural object, since plays the important role in the formation of physical and chemical processes. The uniqueness of water is manifested in the fact that the simple structure of water molecules is in stark contrast to the vast variety of different phases and complex phase diagrams of water. The emergence of the amorphous structure is determined by X-ray diffraction method because the lack of Bragg diffraction in the crystal lattice is a criterion amorphization of substance. The metastable structure of amorphous ice in the conditions of normal pressure was received at a temperature -3^0C. Experimental conditions were described in work [1]. Using Fourier transformation the algorithm of creation of functions of radial distribution was developed for amorphous structure. Functions of radial distribution of amorphous ices have been constructed at temperatures -3^0C and -160^0C comparable to the known functions for water at 1.5^0C [2]. Function of radial distribution of amorphous ice at a temperature -160^0C has been calculated from the diffractogram provided in [3]. Results of such calculations are given on Figure1.

Comparison of radial distribution functions shows that, unlike water, amplitude of electronic density fluctuations of amorphous ices is almost constant. As show calculations, this persistence of amplitude remains on extremely measure to distances 30Å.

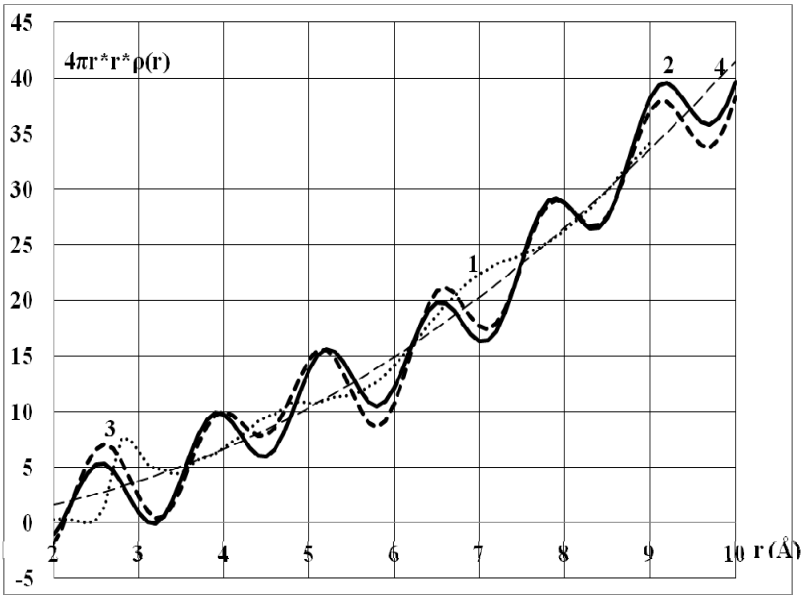

Figure1: Functions of radial distribution: 1) water [2]; 2) amorphous ice -3^0C; 3) amorphous ice -160^0C; 4) $4\pi r*r*\rho_0(r)$ - average value of electron density fluctuations.

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Transport of methyl Oleate in hierarchically structured titaniumsilicalite-1 catalysts probed by means of diffusion NMR

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Diffusion of long-chain hydrocarbons in confined environments remains in the focus of modern science. It is relevant, e.g., in the heterogeneously catalyzed oil cracking, transesterification of oils for biodiesel production or in biodiesel epoxidation. Among the major challenges associated with the utilization of nanoporous catalysts in these type of conversions are diffusion limitations. The latter occur under conditions when the reaction time scale is notably smaller than the time needed for delivery of reactants to the catalytic sites and/or product removal. The diffusion process in such case becomes dominating and determines the overall reaction rate. Thus, obtaining quantitative information on the transport characteristics of long-chain hydrocarbons confined to nanopores is vital.

In the present contribution, we demonstrate the applicability of the pulsed field gradient (PFG) NMR for probing diffusion of methyl oleate ($C_{19}H_{36}O_2$) adsorbed into the mesopore system of post-synthetically treated titanium silicalite-1 (TS-1) at room temperature. This catalyst is known to be highly selective in the liquid-phase oxidation of a wide range of hydrocarbons using aqueous H_2O_2 as the sole oxidant [1]. It is suggested that the introduction of larger (meso)pores might facilitate diffusion of methyl oleate into the crystals of hierarchically structured TS-1. In this context, the main focus of the present contribution is placed on a proof-of-principle demonstration of the direct assessment of self-diffusion coefficients of the long-chain methyl oleate adsorbed within TS-1 possessing the mesopores by means of PFG NMR [2].

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Dynamical instabilities and mass transport in solids surfaces under external stress

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It is well known that in solids under external stress the mass transport rate is several orders of magnitude bigger than in the relaxed state. It is usually accepted that this phenomena is due to a high local stresses, which decrease the activation energy barrier for diffusion. However, the matter transport anomalies are also observed in the surface layer of solids under low applied stresses $\sigma/E \approx 10\text{-}4\text{-}10\text{-}3$ (E is the Young's modulus). In particular, at the Ge (111) surface the pattern with two wavelengths and with two different amplitudes of these waves is formed [1]. This structure is formed at the stage of inelastic deformation under applied stress $\sigma/E \approx 10\text{-}4$. The difference between the patterns formed under low and high stress is related to the lifetime of these structures. In the case of a low stress, the lifetime is finite (from few to tens minutes). If diffusion mechanism of mass transport is assumed, then a diffusion coefficient will be depended on the local curvature of the surface. Therefore the mass transport occurs faster in the zone with larger curvature [2-4]. However, using this model the formation of inhomogeneous structures with the large amplitudes at a short time scale is difficult to explain.

In considered paper a new insight on this problem is proposed. It was shown that taking into account the electron degrees of freedom in the general Hamiltonian allows to explain the high frequency oscillated heterogeneities appearing on the solid surfaces under external stress. It was demonstrated that electron-electron interaction leads to additional dynamic displacements of atoms and, consequently, to an additional mass transport. As example, a semi-infinite homogeneous isotropic one-component solid under uniaxial stress has been considered. In this approach two order parameters have been introduced: first, related to the perturbations of the electronic subsystem and the second described the dynamic atomic displacements. The coupled system of differential equations describing the evolution of the system has been obtained. The detail analysis of the solutions of these equations has been done. It was shown that the resulting short-lived waves can be associated to the damped auto-solitons i.e. localized non-equilibrium states of a system of nonlinear equations. The peculiarities of soliton excitation and the role of the thermal excitations on the matter transport processes at surface layer in solids under stress have been discussed.

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Diffusion-controlled phase transitions as a tool for tailoring Fe-Ga functional properties

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Fe-Ga alloys exhibit unique functional properties such as magnetostriction that can be varied from the highest positive values among iron-based alloys to negative values including zero magnetostriction, if proper compositions and heat treatments are chosen. This remarkable behavior is related to rather complex diffusion-controlled phase transformation sequences in this alloy family that are still unresolved. In earlier studies, the phase transformations in Fe-Ga alloys were studied by X-ray diffraction, which provides structural information limited to the near-surface sample area. In this work, we use electron back-scatter diffraction and *in situ* neutron diffraction to characterize the $D0_3$ and $L1_2$ phases that originate from the fcc and bcc phases in the Fe-27Ga type bulk alloy, respectively. Different ratios between these phases, characterized by magnetostriction values of different signs, were achieved using an isothermal annealing treatment that produces an intrinsic composite in the alloy. Depending on the relative fraction of the $D0_3$ and $L1_2$ phases, the magnetostriction values of the alloy, λ_S, vary from +100 to -50 ppm, including the value of $\lambda_S = 0$ for the alloy with $L1_2$:$D0_3$ = 2:1 achieved after 600 min annealing at 400°C, thus demonstrating the controlled adjustment of magnetostriction in these advanced alloys.

With respect to phase transitions, we demonstrate that the phase transition from a metastable ordered bcc-derivative $D0_3$ phase to an equilibrium fcc-derivative ordered $L1_2$ phase first leads to disordering of the $D0_3$ phase to obtain an A2 structure followed by an A2 to A1 transition with final A1 phase ordering to achieve the $L1_2$ structure. This transition sequence: $D0_3 \rightarrow A2 \rightarrow A1 \rightarrow L1_2$ is proven for the Fe-27Ga alloy at both instant heating and isothermal annealing between 400 and 475°C. Additional doping by Tb stabilizes bcc-derivative phases with respect to heating rate or annealing time and, therefore, fixes structures with high positive values of magnetostriction.

The results of this work present the details of the phase transformations occurring in Galfenol for the first time and they also pave the way for tuning the microstructure of the alloy in such a way that the magnetostriction of the material can be tuned in a controlled way to meet the demands of a given application.

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