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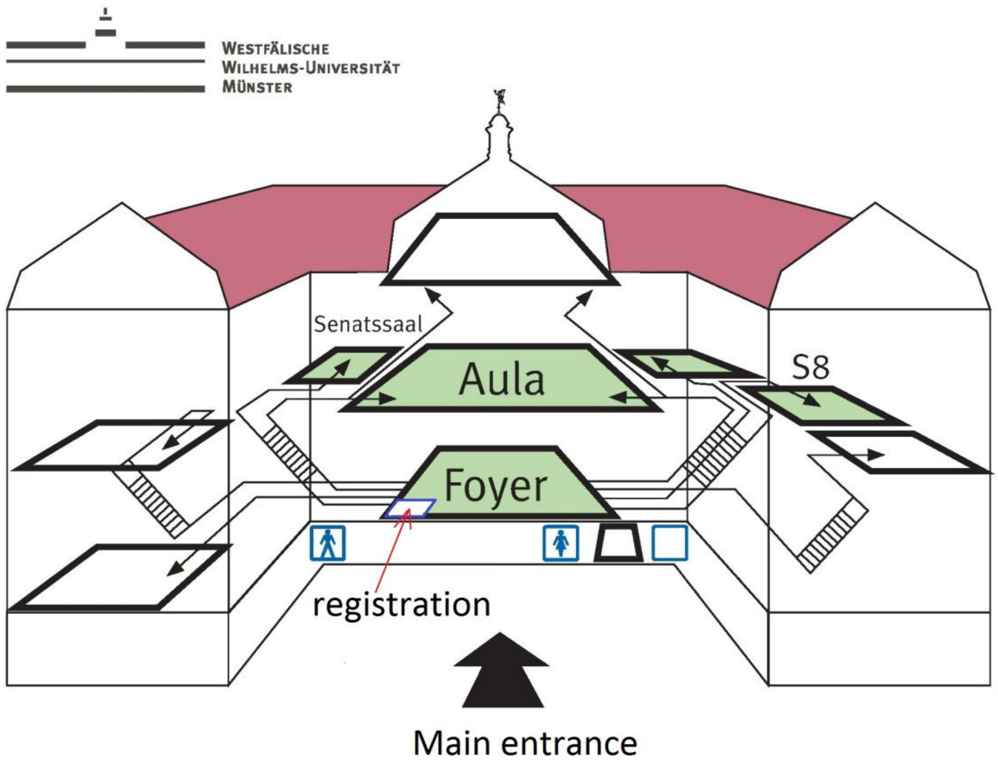
DIMAT2014

International Conference on Diffusion in Materials

Münster, Germany
August 17-22, 2014

Westfälische
Wilhelms-Universität
Münster

CONFERENCE SITE MAP



Room/Location	Function/Event
Registration	registration, daily conference office
Foyer	welcome, coffee breaks, poster sessions
Aula	plenary and invited talks, (parallel) sessions
S8	parallel sessions
Tent behind castle	Lunches, BBQ
Senatssaal	Internation Advisory Board Meeting

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6 August 2014

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PL: Plenary talk (40 min) **I:** Invited talk (30 min) **K:** Keynote talk (25 min) **Oral** contributions : 20 min (all times including discussion)

SCIENTIFIC PROGRAM

time	Sunday, August 17
	Aula
16:00 - 18:00	Registration
18:00 - 20:00	Welcome reception

time	Monday, August 18			
	Aula			
8:00	Registration			
8:30	Opening			
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	Novel techniques and advances in diffusion measurements Chairperson: Y. Sohn		Strong- and micro-gravity materials Chairperson: Z. Erdelyi	
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time	Friday, August 22			
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	Energy storage and energy conversion Chairperson: R. Abart		Diffusion-controlled processes Chairperson: B. Straumal	
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Materials genome for diffusion – oxidation

J. Ågren

Materials science and engineering, Royal Institute of Technology (KTH), Stockholm, Sweden

The over-all aim of the materials genome initiative announced by US president Obama 2011 is “to reduce development time by providing the infrastructure and training that (American) innovators need to discover, develop, manufacture, and deploy advanced materials in a more expeditious and economical way”. The present author introduced the concept of an advanced genome database for the combination of a mathematical model and an accompanying database. Models and databases allowing simulation of diffusional reactions to design new materials thus play an essential role in the materials genome. So far advanced genome databases for diffusion in metallic phases, e.g. in steels, super alloys and light metals, have been developed and are steadily extended to include wider classes of alloys.

Diffusion processes in oxides are much more complicated than in metallic alloys and despite their importance in oxide materials and oxidation of alloys no systematic efforts similar to the ones in metallic systems have been attempted, probably because the high complexity of the problem. Nevertheless, Wagner’s theories for external and internal oxidation are a starting point for such efforts. In the talk the general framework for a genomic approach on oxide diffusion and some recent work on this area will be presented.

The atomistic view of interface diffusion

Y. Mishin

George Mason University, Fairfax, Virginia, USA

Diffusion along internal interfaces controls the kinetics of many processes such as microstructure evolution, phase transformations and solid-state reactions. Many phenomenological models of grain boundary diffusion have been developed over the years, including the Fisher model and its numerous extensions. Significant progress has been achieved in accurate experimental measurements of grain boundary diffusivities. Yet, atomic-level understanding of interface diffusion remains highly incomplete. Most experimental methods provide only macroscopic numbers and little information about diffusion mechanisms. Atomistic computer simulations remain the most efficient tool for gaining fundamental, atomic scale insights into interface diffusion. This talk will present a brief overview of the current knowledge of grain boundary diffusion mechanisms and their relation to boundary structure. Some of the recently found effects include de-localized states of vacancies and interstitials and collective mechanisms of their motion. The most typical diffusive event is a collective displacement of a chain of atoms filling an open space in front of the chain and leaving a new open space behind. Evidence for the existence and dynamic properties of such chains, or strings, obtained by atomistic simulations will be presented. Relationships between diffusion mechanisms and grain boundary structures and structural phase transformations will be discussed.

Guest Diffusion in Nanoporous Solids: Messages for Fundamental Research and Material Science

J. Kärger

Leipzig University, Leipzig, Germany

As an omnipresent phenomenon in nature, diffusion is among the rate-determining processes in many technological processes. This is in particular true for mass separation and catalytic conversion in nanoporous materials [1]. The talk illustrates the possibilities of exploring diffusion phenomena in such "host" materials by monitoring the evolution of guest concentrations by the techniques of microimaging [2]. In this way, transient guest profiles, known from the Crank and Carslaw-Jaeger textbooks become accessible by immediate experimental observation. Examples of insight so far inaccessible include the quantification of transport resistances on the surface of the individual crystallites [3], the exploration of the interrelation between tracer diffusion and chemical diffusion of guest molecules [4], the determination of "sticking coefficients" as a measure of the probability that, upon colliding with the external surface of such materials, gas molecules are able to penetrate into the crystal bulk phase [5] and the observation of guest-induced variations in the host lattice [2] .

[1] J. Kärger, D.M. Ruthven, and D.N. Theodorou, Diffusion in nanoporous materials, Wiley - VCH, Weinheim, 2012.
[2] J. Kärger et al., Nat Mater 13 (2014) 333–343.
[3] L. Heinke, and J. Kärger, Phys. Rev. Lett. 106 (2011) 74501.
[4] C. Chmelik et al., Phys. Rev. Lett. 104 (2010) 85902.
[5] L. Heinke et al. Phys. Rev. Lett. 99 (2007) 228301.

Na^+ Ion Conduction and Diffusion in and Relation to the Structure and Properties of New Mixed Glass Former Solid Electrolytes for Low Temperature Sodium Batteries

Steve W. Martin

Department of Materials Science & Engineering, Iowa State University, Ames, USA

While Lithium batteries have gained great attention as portable energy sources for a range of applications from cell phones to plug-in and hybrid automobiles, the use of such Lithium batteries in electrical grid energy storage for load leaving and peak shifting is coming into question due to the limited natural abundance of lithium. Sodium has long been a low cost alternative to lithium for such large scale battery systems. So far, sodium batteries have been designed to operate at elevated temperatures to resolve problems of low Na^+ ion conductivity in solid electrolyte separators. For this reason, new higher conductivity Na^+ ion conducting solid electrolytes are of great interest and in this research program, we are actively exploring new glass compositions with very high conductivities.

In ternary glasses which are comprised of one modifying salt, typically an alkali oxide, and two (or more) glass formers, the composition dependence of properties such as the alkali ion conductivity is a highly non-linear function of the ratio of the two glass formers at constant alkali oxide concentration. For example, in the ternary system $Na_2O + BO_{3/2} + PO_{5/2}$, the Na^+ ion conductivity reaches a strong maximum nearly two orders of magnitude higher than the linear interpolation between the two end member binary glass formers. Hence, in the sodium phosphate glasses, the role of added boron is to dramatically increase the Na^+ ion conductivity, whereas it is to sharply decrease the Na^+ ion conductivity in sodium silicate glasses. Hence, these ternary mixed glass former glasses provide a unique opportunity to study large and systematic changes, both positive and negative, in the Na^+ ion conductivity caused by the addition at constant Na^+ ion concentration of a single component, in this case $BO_{3/2}$ (B_2O_3).

In the related, but much higher conducting sulfide glass series, the $Na_2S + BS_{3/2} + PS_{5/2}$ mixed glass former system, the Na^+ ion conductivity reaches a sharp maximum corresponding to a rapidly decreasing conductivity activation energy. In the corresponding $Na_2S + GeS_2 + PS_{5/2}$ mixed glass former system, the Na^+ ion conductivity reaches a sharp minimum corresponding to a rapidly increasing conductivity activation energy. These behaviors are shown below in Figure 1.

In this talk, the changes in both structure and properties of these ternary glasses and their dependence concentration will be reported. ^{11}B and ^{31}P MASS NMR measurements have been combined with IR and Raman vibrational spectroscopies and X-ray and neutron scattering measurements further sub-stantiated with Reverse Monte Carlo simulations have been used to develop detailed models of the structures of these glasses. These models have been combined with measurements of both the Na^+ ion conductivity and the physical properties to develop key understandings of the unique role of boron in these ternary glasses.

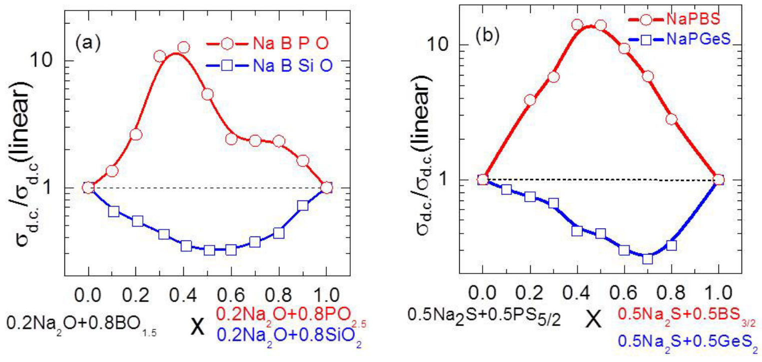

Figure 1 (a). Comparison of the Na^+ ionic conductivity of a positive Na B P O and a negative Na B Si O oxide Mixed Glass Former system and (b) a positive Na B P S and a negative Na Ge P S sulfide Mixed Glass Fomer system.

Diffusion in materials – unde venis, quo vadis

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Atoms in all states of matter are subject to continuous irregular motion, a process that is denoted as diffusion. An important theoretical step in the field was Einstein's theory of Brownian motion. Diffusion studies in solids started with the work of Sir Roberts-Austen, who investigated diffusion in gold in lead and analyzed his experiments using Fick's laws. Georg van Hevesy introduced radioisotopes into diffusion, which permit studies of self-diffusion and solute diffusion free from thermodynamic driving forces. In addition the Boltzmann-Matano method enabled studies of chemical diffusion in alloys. Nowadays self- and solute diffusion and interdiffusion in many elements and binary alloys are well studied. Diffusion studies of metals, semiconductors, ionic conductors, metallic glasses, quasicrystals, intermetallics, ceramics and porous media brought remarkable progress. The same is true for diffusion along grain boundaries in metals.

The question 'diffusion quo vadis' is more difficult to answer. Diffusion in solids is a well-developed field, but it remains an important issue of solid-state physics, of solid-state chemistry, of solid-state ionics, of materials science and even of biophysics. Diffusion and defect properties in nanomaterials, reactive diffusion on the nanoscale, diffusion in porous and confined systems, diffusion in ion-conducting solids especially in Li solid electrolytes and electrodes, diffusion in polymer electrolytes, dopant diffusion in semiconductor alloys, diffusion in ternary and quaternary alloys and intermetallics, diffusion in melts and liquids, diffusion short circuits in thin films, diffusion in grain boundaries of nonmetallic systems, ab initio molecular dynamics and Monte Carlo calculation of defect and diffusion properties, diffusion in biological membranes, the phenomena of electro- and thermomigration and others remain challenges.

The number of diffusion laboratories at this time is unfortunately declining worldwide. Nevertheless, there is a continuing need for good diffusion studies in the future. In my opinion it is one prime task of the diffusion community to keep diffusion science and especially its experimental branch alive.

Ab initio determination of point defects energetics and derived diffusion properties in metals

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Accurate point defect energies are crucial for a reliable simulation of diffusion processes in materials science. While formation energies as function of process conditions such as temperature and chemical potential determine the equilibrium defect concentration, activation energies for jumps of vacancies and interstitial atoms are decisive for their kinetics. Both quantities can be significantly altered by the interaction with other defects.

In this contribution, we will first apply our highly accurate ab initio methods for free energies to vacancies [1]. We will demonstrate that including all relevant free energy contributions yields an highly non-linear temperature dependence, resulting in substantial deviations between low and high temperature results [2]. Further, thermodynamics concepts including defect complexes will be applied to explain the exceptionally high vacancy concentration in FeAl intermetallic alloys and the exciting effect of superabundant vacancies in metals [3]. The insights will be used to determine the dominating self-diffusion mechanism in the B2 phase of FeAl as well as the kinetics of H in steels.

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Interdiffusion in liquid metals measured in-situ

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Chemical diffusion coefficients in liquid alloys are required for modelling of microstructure formation during solidification. They would not only serve as input parameters for modelling but could also be used as benchmark values for molecular dynamics simulations as well as for testing models linking self- with chemical diffusion and diffusivity with viscosity.

In recent years excellent progress has been made by measuring self diffusion coefficients of particular elements in pure liquid metals as well as in binary, ternary and sometimes even multicomponent alloys using neutron scattering techniques. However, for studies of chemical diffusion over broad alloy concentration ranges as well as material classes, capillary experiments remain the method of choice.

The few data available for chemical diffusion in liquids and their large scatter are a direct consequence of additional mass transport of varying origin disturbing the measurements. In order to overcome these problems X-ray radiography has been combined with capillary techniques to observe the diffusion process in-situ.

A detailed description of the new technique is given. Experiments on Al and Ge based alloys are presented. The data are discussed in the framework of models linking self with chemical diffusion and diffusivity with viscosity.

Mn dissolution into Ge (001)

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The Mn-Ge system is highly regarded for integration of spintronic applications in the CMOS technology based on Si and Ge materials. The possibility to create a diluted magnetic semiconductor (DMS) thanks to the incorporation of Mn atoms in Ge is particularly investigated. In this work, we studied the dissolution of 0.5 monolayer of Mn in Ge bulk. Secondary ion mass spectrometry (SIMS) was used to determine the Mn diffusion profiles in Ge, atomic force microscopy (AFM) and Auger electron spectroscopy (AES) were used to characterize the sample surface, and electron spin resonance (ESR) was used to determine the origin of the ferromagnetism signal observed in the Ge(Mn) solution. The study of Mn diffusion shows that the quasi-totality of the incorporated Mn atoms occupies substitutional sites and exhibits at least two negative elementary charges. The solubility limit of Mn in Ge is comprised between 0.7 and 0.9 % for temperatures comprised between 450 and 600 °C. Mn-Ge islands were formed on the sample surface during Mn dissolution. These islands exhibit a ferromagnetic signal, while the incorporated Mn atoms are not ferromagnetic. These results suggest that the magnetic properties of annealed Mn:Ge DMS with Mn concentration ›1% are actually related to magnetic Mn-Ge phase precipitation.

Hierarchy of fast diffusion paths in thin films revisited

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We studied the solid state dewetting of thin Au, Ni and Fe films, and Au-Fe bilayers deposited on sapphire substrates. Both Au and Fe films were nanocrystalline, while the Ni and Au-Fe films exhibited a strong heteroepitaxy to the substrate. The single crystalline particles formed at the late stages of dewetting exhibited stable faceted shapes that were far from those predicted by equilibrium considerations. We discussed high stability of faceted particles in terms of slow mass transport along the singular atomically flat facets. In the case of heteroepitaxial Ni films and Au-Fe bilayers, the formation of faceted pinholes to the substrate is accompanied by the nucleation and growth of twin boundaries parallel to the substrate. These boundaries allow nucleating of defects at the side facets of the pinhole, thus enabling its growth.

We argue that the slow pace of surface diffusion in thin textured films brings to the forefront other types of short-circuit diffusion, such as grain boundary diffusion and metal self-diffusion along the film-substrate interface. We illustrated the importance of these short-circuit diffusion paths in the framework of new quantitative models of solid state dewetting. The predictions of the models were in a good agreement with the experiment.

Anomalous Diffusion Mechanisms and Point Defect Engineering Strategies in Germanium

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Germanium is experiencing a renaissance during the last decade as a potential substitute of Si in advanced CMOS devices due to its superior charge carrier mobilities. However, in order to meet the technological requirements, several issues have to be overcome. In particular it is mandatory to reach an understanding of the diffusion mechanisms of dopants and impurities as well as to develop strategies to control diffusion and defect evolution with a level of detail even higher than what have been reached for the 'brother' silicon after many decades of investigations. After significant progresses done over the last years, the microelectronic industries seem now to consider the implementation of Ge in next technology nodes as a viable option.

In this talk, recent experimental studies on the anomalous diffusion mechanisms and point defect engineering strategies in crystalline Ge will be reviewed. They will involve effects of many different phenomena and processes, such as radiation enhanced diffusion, implanted defects, effects of impurities (implanted or diffusing), clustering, as well as phenomena occurring during ultrafast melting regimes and liquid/solid transitions. The results will depict a complex panorama, with significant differences with respect to what experienced with silicon.

Stress-Strain-Diffusion Interactions in Solids

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The diffusion of elements and vacancies is treated within the framework of continuum mechanics and thermodynamics. The stress-strain-diffusion interactions are mediated by vacancies and different partial molar volumes of elements. Each possible activity of vacancies, determined by their sources and sinks, is incorporated into Manning's theory. The role of stress state is treated and shows its different influence on diffusion of substitutional and interstitial elements as well as of vacancies. Moreover, the stress state influences the vacancy generation/annihilation kinetics causing local swelling/shrinkage and creep, which is well known as Kirkendall effect [1].

The classical concept of Nabarro creep is extended for a general dislocation microstructure and accounts for both mechanical and chemical driving forces. The creep consists in generation and annihilation of vacancies at dislocation jogs acting as non-ideal sources and sinks for vacancies. This mechanism causes the climb of dislocations, allowing for local volume and shape change. The final kinetic equations, relating the dislocation microstructure and the local stress state to the creep rate, are derived by means of the thermodynamic extremal principle. Closed-form equations for the creep rate are derived for isotropic polycrystals [2].

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Reading the memory of rocks: the role of diffusion and diffusion-reaction in microstructure and chemical evolution over geological time scales

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Phase content, mineral compositions, microstructure and texture provide key information on rock forming processes. Many mineral reactions involve composition change and thus represent diffusive phase transformations. We address three types of diffusion controlled mineral reactions and derive constraints on the dynamics of geological systems. In a first example we investigate diffusion controlled composition change in a single crystal triggered by a sudden change of the contact conditions at its surface. To this end, we determine the duration of heat pulses from the diffusion profiles developed in olivine and pyroxene during partial melting of the HED meteorite Yurtuk. In a second example the rate of a dehydrogenation-oxidation event is estimated from diffusion profiles accompanying symplectic pyroxene-spinel precipitates in lunar olivine. The third example is devoted to exsolution in alkali feldspar. Alkali feldspar is a binary solid-solution between a sodium and a potassium end-member, which are completely miscible at high temperature and tend to exsolve during cooling. We model exsolution using Cahn-Hilliard theory and present an experimental calibration of Na-K interdiffusion, which reveals pronounced composition dependence, anisotropy and coherency effects arising from the composition dependence of the lattice parameters. Finally, we address myrmekite formation, a mineralogical case of discontinuous precipitation.

Reactive diffusion on the nanoscale: phase nucleation and growth in sharp concentration gradient

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Phase nucleation and growth in sharp concentration gradient have been investigated in Ni-Si and Co-Si systems. We show how a combination of experimental methods of XRD (x-ray diffraction), 4-wire resistance, GIXRF (grazing incidence x-ray fluorescence) analysis and EXAFS (extended x-ray absorption fine structure) spectroscopy in fluorescence detection with x-ray standing waves (XSW) technique was applied for the depth profiling of a-Si/Ni/a-Si and a-Si/Co/a-Si layers with nanometer resolution to monitor the growth of Ni_2Si and CoSi phases. We observed that a mixture of Ni and Si with 2:1 composition ratio is formed at the interfaces during sample preparation, but its thickness was different at the a-Si/Ni and Ni/a-Si interfaces. During annealing Ni_2Si crystalline phase formed but surprisingly the thicker Ni_2Si layer grew faster than the thinner one. We found similar peculiar behaviour in the a-Si/Co/a-Si. To clear up this and to understand better the phase formation and growth process simulations have been performed by using our new conceptual model [Erdélyi at al. Acta Mater. 2012;60:1807], in which thermodynamic driving forces are included to model formation of intermetallics. This showed that the thickness of the interfaces and the accelerated diffusion in the intermetallic phase (total mixing nucleation mode) presumably play key roles.

Mechanical mixing and solute redistribution in severely deformed metallic alloys

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Metallic alloys may be subjected to large levels of plastic deformation in various situations: during forming processes, surface treatment (shot peening), in service (contact wear), powder processes (ball milling) or in so-called "Severe Plastic Deformation" processes used to obtain UltraFine Grained materials. The large amount of crystalline defects created during the plastic deformation, may significantly enhance the atomic mobility leading in some cases to the formation of super saturated solutions by mechanical mixing or vice-versa it may promote the decomposition of solid solutions via dynamic precipitation. In this talk, we propose to review these phenomena on the basis of some experimental work carried out on various model systems deformed by High Pressure Torsion and characterized at the atomic scale using a combination of Atom Probe Tomography and analytical Transmission Electron Microscopy. It will cover first the forced interdiffusion in the immiscible Cu-Fe system and in an Al-metallic glass composite. The second part will be devoted to the accelerated decomposition of solid solutions in aluminium alloys and the formation of non equilibrium segregations. In both cases, a special emphasis will be given on atomic scale mechanisms, and especially on the role of lattice defects created during the deformation like dislocations and vacancies.

Defect Studies in Ultrafine-Grained and Amorphous Metals with Dilatometric Techniques

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In novel, high-performance metallic engineering materials, such as ultrafine-grained (UFG) metals or amorphous metals, basic physical properties and diffusional processes are, to a large extent, determined by volume-type atomic defects and their kinetics. These defects comprise vacancies, dislocations, and unrelaxed and relaxed grain-boundaries in the case of ultrafine-grained metals, obtained, e.g., by severe plastic deformation (SPD), and volume-type defects in the case of bulk metallic glasses. The absolute concentration of these defects can be determined, and their kinetics can specifically be analyzed using macroscopic dilatometric techniques [1]. High-precision difference-dilatometry was used for the study of UFG fcc and bcc metals after SPD processing, e.g., to determine the absolute concentrations of free-volume type defects [2], to characterize grain growth processes [3, 4], and to determine the grain boundary excess volume [5,6]. For bulk metallic glasses thermally activated, reversible formation and disappearance of specific volume was studied in a temperature regime far below the calorimetrically determined glass transition temperature employing time-dependent, high-resolution LASER-dilatometry [7]. The results will be discussed with respect to specific diffusion processes in both types of materials. Financial support by the Austrian Science Fund (FWF) is appreciated (P21009-N20, P22645-N20).

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Grain boundary diffusion induced solid state reactions and linear-parabolic growth in nanostructured thin films

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We have illustrated in a series of low temperature experiments (where the bulk diffusion processes are frozen) in different thin film systems that even fully homogeneous phase(s) can be formed by cold homogenization called Grain Boundary Diffusion Induced Solid State Reaction (GBDIREAC). First the reaction starts by grain-boundary, GB, diffusion and nucleation of the new phase at GBs or their triple junctions, then the growth of the new phase happens by the shift of the new interfaces perpendicular to the original GB. This is a process similar to the DIGM or DIR phenomena and in this case the interface shift, at least in the first stage of the reaction until the parent phases have been consumed, can be considered constant. This means that the amount of the phase increases linearly with time, giving a plausible explanation for the linear kinetics frequently observed in first stages of solid state reactions in thin films.

Simultaneous measurement of tracer and interdiffusion coefficients in a diffusion couple

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In this paper, a new exact formalism of isotopic diffusion in an interdiffusion context is described. It is based on the Onsager phenomenological theory and linear response theory. The resulting expressions in the laboratory frame are surprisingly simple and consist of terms coming from the standard interdiffusion expressions and from Fick's first law where the tracer diffusion coefficient is involved. A sandwich type of interdiffusion experiment is most successful for the application of this formalism. The interdiffusion couple should initially contain a thin tracer layer of one or both of the constituent elements at the interface of the two parts of the couple. This type of experiment was first performed in 1958 by the late John Manning but never analysed in terms of tracer diffusion. The new formalism provides the means to obtain the interdiffusion coefficient and tracer diffusion coefficients simultaneously from analysis of the interdiffusion and tracer profiles. It was very successfully applied to the results of Manning's experiment in the Ag-Cd system (6 couples in total) and compared with independent measurements of the composition-dependent tracer diffusivities. Further development of the sandwich interdiffusion experiment and analysis to the case of multicomponent alloys will be commented on.

Capillarity in Solids: 1D Structural Elements of Polycrystals and Stability of Grain Microstructure of Nanocrystalline Materials

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The presentation is dedicated to the thermodynamics and kinetics of 1D structural elements of polycrystals – grain boundary and interfacial junctions and their role in grain microstructure evolution and stability of nanocrystalline materials. The interaction between inclusions and grain boundaries is one of the major phenomena which affects the grain microstructure evolution and, as a consequence, the stability of fine grained and nanocrystalline materials. Although the retardation of grain boundary motion and grain growth by small particles in polycrystals is known for more 60 years (so-called Zener drag), recent studies have shown that the influence of interfacial triple junctions on this interaction for small particles and voids exceeds significantly classical Zener estimations.

A recently introduced correct thermodynamic approach makes it possible to experimentally determine the grain boundary and interfacial line tension and, as a result, to reestimate the Gibbs-Thomson relation, the driving force for grain growth in nanocrystalline materials, and to better understand the process of coalescence of small inclusions at grain boundaries that is especially important for fine grained and nanocrystalline materials.

Chemical Effect on Grain Boundary Diffusion in Solids

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In the case of heterodiffusion chemical interaction between the different components in grain boundary (GB) solution must be taken into account. The most important effect of chemical interaction on GB diffusion (GBD) is the segregation of solutes at GB – GBS. The simplest model of GBS effect on GBD was proposed by Gibbs who supposed the linear dependence between GB and bulk concentrations and introduced the segregation coefficient "*s*". Unfortunately the Gibbs solution does not describe such effects as nonlinear segregation profiles, the ambiguity of *s*-dependence on material purity, etc. Hence, the following effects were analyzed: limited number of segregation cites in GB, nonideality of GB solution (in frame of regular solutions theory) and GB inhomogeneity.

Two strong effects which can be used to describe the retardation of GBD are under discussion:

- atomic complexes formation at GB with chemical composition and interatomic bonds similar to the nearest bulk phase in phase diagram;
- "poison" effect in the systems with strong repulsive interatomic interaction.

Experimental and MD simulation data which confirm the effects will be presented.

Grain-boundary diffusion of Co in Mo studies by radio tracer and Mossbauer spectroscopy techniques

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In [1] we suggested a specification of Fisher's model of grain-boundary diffusion. Our model speculates that monatomic layers of equilibrium concentration of a diffusing component are adjacent to grain boundaries. In [2] this model was applied to the treatment of the radio tracer and the emission Mossbauer spectroscopy data on grain-boundary diffusion of Co in W.

In this study this approach is developed by an example of grain-boundary diffusion of Co in Mo. Based on the Mossbauer data, it is demonstrated that mass-transfer proceeds by interstitials. The temperature limit of the kinetic type C regime and temperature dependence of segregation factor s have been determined. Based on the radiotracer data for low-temperature range, the temperature dependence of grain-boundary diffusivity, D_b, is obtained in view of the temperature dependence of s. For the high-temperature range the temperature dependence of the triple product $s\delta D_b$ (where δ is a grain boundary diffusion width) has been determined and $s(T)$ has been calculated. $s(T)$ obtained from diffusion and Mossbauer studies are compared.

The work is supported by Ural Branch of RAS (project No. 12-P-2-1016) and RFBR (project No. 14-03-31596).

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Grain boundaries in severely deformed metallic materials

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Materials with a high specific area of internal interfaces possess properties that can significantly deviate from the properties of their polycrystalline counterparts. Processing of sufficient quantities and enhancing the stability of the fine grained microstructures, once obtained, against coarsening are long-standing issues in this context. Within the past decade, severe plastic deformation (SPD) has often been applied for refining the microstructure of polycrystalline materials down to the submicron (the “ultrafine grained”) – or even the nanocrystalline grain size range, yielding bulk materials that are mostly free from porosity or contaminations of the internal interfaces. At the same time, materials that were processed by severe deformation routes showed remarkable property modifications that exceed the modifications due to the mere presence of the total area of internal interfaces.

Thus, it seems straight forward to assume that the severe deformation processing introduces additional structural changes besides enlarging the total grain boundary area. In fact, already early on in the research concerning SPD-processed materials, corresponding theoretical models have been constructed that e.g. advocate the existence of so-called “non-equilibrium” grain boundaries that have been modified due to the interaction of random high angle grain boundaries with the abundant lattice dislocations that are generated during the severe deformation. Such “deformation-modified” grain boundaries should possess enhanced excess free energy densities, enhanced residual microstrain and enhanced atomic mobility along the boundary plane; they might be susceptible for enhanced solute segregation and are supposed to present the microstructure element that underlies the property enhancement. In fact, their presence, their structure and particularly their strain state is of importance for the stability, the mechanical performance and, apparently, also for selected functional properties of these materials, including the grain-boundary diffusion of ultrafine grained materials obtained through severe deformation processing.

In order to address the structural modifications due to SPD processing experimentally, several different pure metals have been analyzed by combining microstructure analyses on different length scales with measurements of the grain boundary diffusivity, since diffusion measurements using radiotracers are highly sensitive for modifications of the interatomic potential and thus the atomic structure, e.g. along fast diffusion pathways such as grain boundaries. Additionally, effects due to the purity of the material as well as the impact of the strain path have systematically been addressed. The present contribution will summarize these results and discuss possible scenarios concerning the correlation between SPD processing and the resulting modifications of microstructures, grain boundary diffusion characteristics and macroscopic materials properties.

Microgravity Science - the previous experimental results and its future prospect

Shinichi Yoda

ISAS/JAXA, Japan

Many experiments have been done in the field of Fluid Physics, Combustion as well as Material Science by using microgravity condition obtained such as International Space Station, recovery satellite and so on, to make clear fundamental aspects of the several kinds of phenomena so far. Microgravity provides us no convection, no hydrostatic pressure, no sedimentation and containless condition. By using those phenomena we have done many kinds of experiments, especially microgravity in the field of combustion, fluid physics as well as material science such as solidification, crystal growth, composite material production and so on, several kind of experiments have been done by using sounding rocket, recovery satellite and International Space Station. In one of conclusion regarding to flame combustion, droplet flame propagation behavior has been studied and made clear formation of vaporized area of materials in the front of flame could decide flame propagation behavior. In fluid physics 50mm diameter liquid bridge successively formed under microgravity condition and surface tension driven flow mechanism has studied so far in ISS. Electro static levitator has developed for JEM as the next generation experiment hardware. It is expected that thermo-physical properties in many kind of material such as surface tension, viscosity and so on, can be measured under containerless condition which can provide high precise value. This hardware can also be expected to study metastable phase formation which is strongly related to new functional material production. The microgravity experiments now are implemented by world-wide research team consist of Asian, Europen, and US scientists, called as International Topical Team. At present, these ITTs are around 10 in the field of combustion, fluid physics, and material science. Those activities will be also reported.

Recent progress in materials science under strong gravitational field

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Gravity is a field state variable that directly acts on atoms in materials by a body force, while pressure and temperature are thermodynamic state variables that influences atoms isotropically. So, strong gravitational field causes atomic displacement and sedimentation of atoms in solids through body force, by which we can changes the crystalline state and composition in multi-components condensed matter, although a microgravity field has been used to suppress the effects of gravity. We have developed a high-temperature ultracentrifuge to generate a strong acceleration field of even over 1 million (1×10^6) *G*, and, for the first time, succeeded in realizing of the sedimentation of the constitutive solute atoms in a solid. The composition changes, graded structure and reactions in various alloys, polymers, and some compounds have been realized. We also succeeded in realizing the sedimentation of isotope atoms and doping of impurity in semiconductors. In addition, recently we succeeded in realizing of structure changes in some oxides due to the displacement of atoms. It is expected that strong gravitational field will be used as a new materials processing to control compositions, nanostructure, impurities and interface, and to synthesize new materials. In this talk, the basics of strong gravity science are reviewed, and recent progress and the future prospects for materials processing are described.

Proton diffusion in solid oxide fuel cell electrolytes

Y. Yamazaki

Japan Science and Technology Agency, California Institute of Technology

Similar to hydrogen in metals, protons exists in oxides, typically doped perovskites. Upon exposure to moisture, the perovskite oxide incorporates hydroxyl groups with replacement of oxygen vacancies. Proton rotates around the oxygen and hops to the neighboring oxygen site. Such proton diffusion technologically plays an important role as an electrolyte for solid oxide fuel cells. The degree of proton diffusivity further defines the operation temperature of fuel cells. Despite its critical importance, macroscopic proton diffusion mechanism in the oxides was under debate since the discovery of proton-conducting oxide in 1981. A specific question was the impact of proton trapping on proton diffusion. Combining electrochemical spectroscopy and thermogravimetry, we have demonstrated that the Arrhenius plot of proton diffusivity curves downward, which is a strong indication of proton trapping. Proton must overcome the association energy, 29 kJ/mol, as well as the general activation energy, 16 kJ/mol, to achieve long-range diffusion. Proton nuclear magnetic resonance also shows the presence of two types of protons environment, reflecting the difference in proton-dopant configurations.

Chemical Diffusivities and their Hidden Concentration Units

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When chemical diffusivities of binary alloys are measured from diffusion couples using the Boltzmann-Matano analysis, they are independent of concentration units and have SI units of m^2/s. However that is not the case for chemical diffusivity matrices of alloys containing three or more components. Their values do depend on concentration units. The matrix units of m^2/s do not reflect that dependence and therefore, in a sense, the concentration units are hidden. It is proposed that concentration units be added to the name of experimental and predicted multicomponent diffusivities, for example "mole fraction diffusivity" or "mass density diffusivity" to alert users to the concentration units that must be used when solving the diffusion equation. It is shown that when partial molar volumes are constant that the multicomponent chemical diffusivity with different hidden units are linearly related. An example will be given of six chemical diffusivity matrices for an experimental Ni-4at%Cr-6at%Al-4at% Mo alloy at 1100°C.

Interdiffusion processes in intermetallics: atomistic Monte Carlo simulations

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We summarize various concepts for addressing the problem of atomistic Monte Carlo (MC) simulation of vacancy-mediated interdiffusion in intermetallic binary systems. Following previous work on self diffusion and ordering kinetics, the role of vacancy thermodynamics is strongly emphasized. Systems with a tendency for “triple-defect”-type disordering, where the very high vacancy concentration enables effective KMC simulations, are investigated using temperature-dependent vacancy concentrations. Two alternative concepts for the simulations are run with the vacancy concentration in the system equilibrated by means of the Semi-Grand Canonical MC (SGCMC) technique either initially (according to the average composition of the diffusion couple) or locally ‘on-line’ during the diffusion process. In addition to the main analysis, the evolution of steps on the crystal surface is also simulated and discussed as a specific case of interdiffusion in a binary metal-vacancy system.

Stability and kinetics of Se overlayers on Mo (110) from first principles: the influence of Na and O

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The selenization of molybdenum is nowadays technologically relevant for the production of thin film chalcopyrite solar cells based on CuInxGa(1-*x*)Se$_2$ (CIGS) and might become an important step in the production of nanostructures based on the layered compound MoSe$_2$. However, the control of the process is still very poor, due to the lack of basic knowledge of the surface thermodynamics of the system. The kinetics, moreover, can become crucial to obtain preferred textures and, thus, electronic properties.

In the case of solar cells the role of sodium impurities, and maybe oxygen, has been invoked, claiming that it could help the formation of an Ohmic contact. Based on first principles calculations of adsorption energies and migration energies of Se, Na, and O on the Mo(110) surface we predict stable patterns for adsorbed Selenium – or surface selenides – for various ambient conditions (temperature, pressure and composition of Se gas). In order to shed light on processes occurring out of equilibrium we use our first principles data in combination with kinetic Monte Carlo simulations, especially to better understand the role of Na and O on the surface kinetics of the system.

Diffusion-Exchange experiments to study chain permeation through nanopores

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Polymeric capsules are prepared by Layer-by-Layer assembly of polyelectrolytes on colloidal particles and subsequent core dissolution, yielding hollow capsules with a several nm thin wall, consisting of an electrostatically cross-linked network. Permeation processes through this wall are essential for encapsulation applications. Here, we study the permeation of polymer chains through the wall employing observation time-dependent Pulsed Field Gradient (PFG-) NMR diffusion experiments. In the regime of intermediate exchange diffusion echo decays are described by a two-site model of exchange between the interior and the exterior. A global fits yields the exchange rate.

The results show that permeation is not controlled by chain diffusion through the wall material, but rather through nm-sized defects, which arise upon core dissolution. Permeation rates are thus controllable by post-preparative coating with additional layers. The dependence of permeation rates on layer number and on chain molecular weight is analyzed. In addition, deviations from the two-site exchange model with one defined exchange rate are found and attributed to a finite width of the distribution of exchange rates. Additional information about this distribution is obtained by analysis of data sets with the upper and lower limit of observation time as a variable parameter.

Lithium Transport through Ultrathin Silicon Layers

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The contribution presents a novel neutron reflectometry based approach to measure non-destructively lithium transport parameters through nanometer sized solid state layers. Such experiments are interesting for research on nanostructured electrode materials in lithium based batteries, Li ion selective electrodes, and sensors. The methodology is demonstrated for 10 nm thin amorphous silicon layers (a high density anode material in Li-ion batteries) covered by solid Li tracer reservoirs. A multilayer with a repetition of five [Si / $^{nat}LiNbO_3$ / Si / $^{6}LiNbO_3$] units is used for analysis. Two types of Bragg peaks are detectable in the reflectivity pattern. One originates from $LiNbO_3$/Si chemical contrast, the other from $^{6}Li/^{7}Li$ isotope contrast. Diffusion annealing reduces only the intensity of second type of Bragg peak, demonstrating that this decrease is a measure of the ^{6}Li and ^{7}Li isotope exchange through the Si layer.

These results open the possibility to determine the rate determining step (diffusion controlled or interface reaction controlled) of the Li transport process and to quantify Li transport parameters (diffusivity and permeability) in nanometer thin layers.

Atom probe tomography of solid state ion-conductive membranes

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Atom probe tomograghy is a technique to study the composition of a tip shaped sample and to reconstruct the three-dimensional arrangement of individual atoms, but it bears a leak of understanding in some fundamental processes. The influence of the laser on the field evaporation, whether it is local heating or electronically coupling is not fully understood, as well as the interaction of laser light with dielectric materials, which are transparent for the used wavelength. Performing atom probe tomograghy on ion-conducting thin films gives some insight in these issues.

The measurements of lithium silicate glasses show a redistribution of Li during the analysis due to electromigration. Hence, the mobile ions act as a probe for the electric field distribution in the thin film during the measurement. The scale of the redistribution gives a possibility to determine the temperature during the measurement as it is a thermal activated process. To extract this information from our data, we simulated the redistribution of Li during the analysis assuming a band bending as predicted by Tsong [1]. Then, we compared these results with our measurements.

[1] T.T. Tsong, Surface Science 82 (1979) 28-42

Interdiffusion in gold-tin system during thermo-compression and eutectic bonding for hermetic packaging at wafer level

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Au-Sn eutectic alloy is the solder of choice, with no obvious alternatives, in many microelectronic applications. Recently, it has been chosen as a potential candidate for bonding in wafer level hermetic packaging at high temperature using W_2N as diffusion barrier. Thus, good wetting of W_2N by the liquid Au-Sn alloy is a key factor for the bonding process and to this end, wetting of W_2N (covered or not by an Au layer) by this alloy was first studied at 380°C under high vacuum. The initial parts of bonding system are: the cap side (cap wafer/W_2N/Au/Sn) and the device side (device wafer/W_2N/Au). The interdiffusion at Au/Sn interface in the cap/W_2N/Au/Sn system that occurs during deposition, storage at room temperature or during heat treatments, leading to the equilibrium state (cap/W_2N/Au_5Sn/AuSn), was studied. Afterwards, thermo-compression and eutectic bonding experiments were performed under vacuum or under nitrogen. The interdiffusion at AuSn/Au interface in the cap/W_2N/Au_5Sn/AuSn/../Au/W_2N/device system, leading to the growth of Au_5Sn compound at this interface, was studied at 270°C for reaction times varying from 20 minutes to 9 hours and for different initial thicknesses of deposited Au layer at the device side and a mechanism of interdiffusion process is proposed.

Effect of Ti on the growth kinetics of A15-based Nb3Sn and V3Ga compounds

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Nb_3Sn and V_3Ga have superior magnetic field (>10 T) than that of Nb-Ti superconductors (8 T). These are brittle in nature; hence bronze technique is adopted to fabricate such filamentary wires. This is based on solid-state diffusion where A_3B compound (A = Nb or V, B = Sn or Ga) forms during the interaction of Cu(B) and A. Elemental addition to either bronze or metal is proved to improve the superconducting properties. Among these, Ti is regarded to be the most effective one. Our objective is to examine the Ti-effect on the metallurgical aspects of A15-phase formed in Cu(B,Ti)/A and Cu(B)/(A,Ti). In either cases Ti-addition results in an improved growth rate of the product phase and reduces activation energy, for Cu(B,Ti)/A, few precipitates are formed in the interdiffusion zone. WDS-mapping reveals these to be Ti-rich. STEM-analysis suggests having composition gradient inside a single precipitate. TEM-diffraction demonstrates these to be Ti(A) solid solution crystallizing as BCC-structure. These are located on grain boundaries of A15-phase. EBSD-analysis demonstrates grain morphology of product phase. Columnar grains, on Ti addition tend to form as equiaxed ones. Based on the morphology, role of grain boundary and lattice diffusion is discussed considering the possibility of increased grain boundary area and point defects.

Diffusion-controlled stability of NiAlPt coating on single-crystal nickel base super-alloy: cross diffusion-stress effect

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Microstructural stability of NiAlPt coating deposited on a single-crystal nickel base super-alloy was studied in isothermal conditions (at 1100 °C) and on thermal cycling with soaking at the same temperature. In initial state due to fabrication process the coating is covered by thermal grown oxide and the interdiffusion zone is observed between the coating and super-alloy substrate. Different behaviour of microstructural evolutions of the coating are observed during the heat treatment depending on experimental conditions: while in isothermal conditions transformation of the coating into the gamma' phase occurs continuously enlarging the interdiffusion zone from the super-alloy substrate, the cycling favours precipitation of gamma' phase on initial NiAlPt grain boundaries and close to the thermal grown oxide/coating interface. Diffusion concentration profiles of alloying elements in the coating are measured by energy dispersive spectroscopy as a function of depth and time. Using microstructure observations, as well as concentration measurements, the difference in NiAlPt coating stability in isothermal and cyclic conditions is suggested to be due to stress generated on thermal cycling. The principal stress effects (mobility-stress, flux-stress and vacancy-stress) on diffusion in NiAlPt coating are analysed and their significance is estimated.

Lithiation of Amorphous Silicon Electrodes in Lithium-Ion Batteries: Kinetics and Diffusion

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Lithium-ion batteries are widely developed and used as rechargeable power sources for portable electronic devices and will be essential in the field of automotive transportation. Kinetics and diffusion processes at/in electrodes during charging and discharging cycles play a key role for an understanding and optimization of these batteries, especially concerning charging rates and power density. We present experiments on galvanostatic lithiation of high capacity amorphous silicon electrodes done by in-situ neutron reflectometry and ex-situ secondary ion mass spectrometry. The combination of these methods allows to obtain information on the kinetics of volume expansion and on the lithiation mechanism. Our results are in agreement with the assumption of a heterogeneous two phase mechanism, where an amorphous moving phase boundary penetrates the electrode at certain potentials Li vs. Li+. Possible explanations for such a behavior based on Li diffusion properties of silicon and of the lithiated Li_xSi phase are presented, which are supported by recent tracer diffusion studies.

Revealing low temperature defect activity of doped ceria for catalytic applications

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Ceria with different dopants has been proposed as catalyst material for various applications due to its high oxygen buffer capacity at temperatures as low as 20 °C [1].

Research was conducted with acceptor-doped ceria ($Ce_{1-x}M_xO_{2-x/2}$ with M = Gd, Pr, Y, Sm) single crystals, thin films, and pellets. Using an AFM cantilever as electrode, samples were polarized at 20/50 °C in air.

The polarization introduces a local defect concentration gradient, exhibiting a decrease of the surface potential with negative or an increase with positive voltage application. The size, intensity, and time-dependent decay of the defect concentration gradient is linked directly to bulk/grain boundary ratio and dopant concentration of the sample.

After polarization, the decay with time of the defect concentration gradient was measured by fast scans of the surface potential in the polarized zone using Kelvin probe force microscopy [2]. These measurements permit to visualize and quantify the role of defects for low temperature redox processes, which is of great value for evaluating and modeling catalytic activity of ceria compounds.

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[1] Vivier et al., Chem. Sus. Chem. 3 (2010) 6.
[2] Lee et al., Nanotechnology 20 (2009) 1.

Lithium Ion Diffusion in Sulfide-based Solid Conductors studied by Pulsed-Gradient Spin-Echo NMR Spectroscopy

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Sulfide-based solid conductors $(Li_2S)_n(P_2S_5)_{1-n}$ are known to have large ionic conductivities (10^{-4} to 10^{-3} Scm^{-1}) at room temperature, and applications to solid lithium batteries are attempted. Since the anions do not contribute ion conduction, the lithium ion transfer can be assumed to determine the ion conductivity. The lithium ion displacements are studied by the pulsed-gradient spin-echo (PGSE) NMR methods, where three measurement parameters can be varied, i.e. observation time, pulsed-field gradient (PFG) strength and its duration time. When a system is homogeneous, the lithium diffusion constant is independent of these measuring parameters and has a single definite value at each temperature.

For the lithium ion displacements in the solid conductors, we observed significant dependence on observation time and also unexpected PFG strength dependent lithium displacements. When the observation time becomes shorter, faster lithium displacement can be observed. With the larger PFG strength, the slower lithium displacement appeared. The lithium diffusion is distributed in a dispersive manner. For longer observation time, although limited by short T2 and T1, the lithium displacements approached to somewhat uniform behaviors.

Next Chapter of Diffusion Couple Experiments: Materials Genome Development

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Understanding of solid-state diffusion through experiments has played a critical role in development of alloys and surface modification for a variety of applications. In this talk, recent experimental diffusion studies in Mg-, Ni- and U-alloys for the determination of thermokinetics and kinetic coefficients are highlighted with respect to a variety of applications including automotive structure, magneto-caloric refrigeration, and low-enriched nuclear fuels. These experimental studies provide excellent hands-on educational tools for both undergraduate and graduate students, and contribute to the alloy development with coefficients of tracer diffusion, intrinsic diffusion, vacancy wind parameters, interdiffusion, and heat of transport. Development of concentration gradients, phase constituents and microstructure are presented along with recent development in miniaturized techniques via focused ion beam for assessment of crystallographic, mechanical, magnetic and thermodynamic properties. A potential role of this classical experimental method for materials genome database development will be presented.

Interdiffusion in epitaxial single-crystalline Ag/Au bilayers

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Thin films often possess high intrinsic stresses and thus they are appropriate systems for studying the interplay of (volume) diffusion and stress caused by insufficient vacancy sources and sinks. However, interdiffusion in polycrystalline thin films can be orders of magnitude faster than in bulk specimens, which can be related to the more defective microstructure. Therefore, for the investigation of volume diffusion in stressed thin films, high quality single crystalline thin films are needed to avoid short circuit diffusion along grain boundaries. In this study epitaxial single-crystalline Ag (160 nm)/Au (100 nm) bilayers (as verified by X-Ray diffraction) with a sharp interface have been prepared on Si(001) substrates by thermal evaporation. The concentration-depth profiles after diffusion annealing in the temperature range from 240°C to 350°C have been measured by Auger Electron Spectroscopy sputter-depth profiling and corrected for sputter induced alterations by applying the Mixing-Roughness-Information depth model. The results obtained show that the self-diffusion coefficient of Au is larger and the self-diffusion coefficient of Ag is smaller, than those presented in literature for bulk specimens. This can be related with the establishment of a nonequilibrium vacancy concentration-depth profile upon interdiffusion, as suggested by positron-annihilation measurements, also carried out in this project.

Modelling interdiffusion processes in a Ni – CMSX-10 joint

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A diffusion couple between polycrystalline nickel and the single crystal Ni-base superalloy CMSX-10 was produced by hot pressing in vacuum and subsequently heat treated at 1050-1250 °C. The exposed samples were characterized by SEM/EBSD/EPMA. The interdiffusion results in dissolution of the gamma prime (Ni_3Al) phase in the superalloy and in growth of nickel grains towards CMSX-10. Rapid diffusion of aluminum from the superalloy into nickel leads to a significant formation of pores in the interdiffusion zone.

Interdiffusion processes were modelled using the finite-element simulation software DICTRA with the databases TCNi5 and MobNi2, tailored specially for Ni-base superalloys. The effect of alloying elements on the interdiffusion profiles is discussed in terms of the CALPHAD method. The calculated element concentration profiles are in good agreement with the EPMA measurements. The simulation predicts an anomalous interdiffusion behavior of aluminum, i.e. a virtually uniform concentration profile in the vicinity of the original interface in the joint. The calculation predicts with reasonable accuracy the extent and the location of the Kirkendall void formation.

Modeling of phase competition in Cu- liquid Sn and Ni-Al systems

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The following results are presented:

1. Modeling of nucleation and growth of Cu_6Sn_5 and Cu_3Sn phases in copper-liquid tin interaction is presented, taking into account wetting of grain boundaries and various nucleation modes.

2. CALPHAD-based modeling of Ni-Al metastable phase diagram in absence of intermetallic phases is presented. Possibility of contact melting at temperatures over 700 K is predicted.

3. Results of Ni-Al MD-modeling by Baras and Politano [1] are confirmed for the case of pure Ni-pure Al immediate contact.

4. Deposition of Ni over Al and Al over Ni at various conditions is modeled.

5. Results of Ni-Al interaction in thin-film couple or in multilayer are shown to depend on the conditions of deposition

[1] F Baras, O Politano, Phys. Rev. B, 84 (2001) 024113.

Effect of Pt in the interdiffusion of β- (Ni,Pt)Al bondcoat with René N'5 Superalloys

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β-(Ni,Pt)Al is one of the favorable bond coats used in hotter section of the jet engine. They provide high temperature oxidation resistance and improved adhesion. Pt addition to β-NiAl is believed to increase the service life by increasing the growth rate of Al_2O_3 layer and decreasing sulfur segregation. Present study examines the effect of Pt on the growth kinetics of β-NiPtAl phase using β-$(Ni,Pt)_{40}Al$/β-$(Ni,Pt)_{50}Al$; each with fixed Pt content (0, 5, 10 at.%) in both the end-members so that the Pt content remains constant throughout the interdiffusion zone (IDZ). The result shows that, the interdiffusion coefficient increases with increase in Pt content. Theoretical studies indicate that Pt addition to β-NiAl decreases the defect formation energies thereby increasing the diffusion rate. Effect of Pt in the growth of topologically close packed (tcp) phases and β-NiPtAl phase is investigated in β-(Ni,Pt)Al/RenéN'5 superalloy. Layer thicknesses of the β-NiPtAl phase and the tcp precipitates increase with increase in Pt content. Increase in Pt content changes the morphology of the tcp precipitates from rod shape to more of spherical. WDS-mapping reveals the presence of two types of tcp phases in the IDZ. From the SAD pattern, the tcp phases were identified as mu-phase and P-phase.

Diffusion pattern in disilicide in group IVB and VB refractory metal-silicon systems

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Group IVB and VB refractory metal-silicon systems are considered to show an interesting pattern in the diffusion of components with the change in atomic number in a particular group. Group IVB metals are Ti, Zr and Hf, whereas, Group VIB metals are V, Nb and Ta. Growth of the phases in an interdiffusion zone is first discussed in general. The location of the marker plane for the estimation of the relative mobilities of the components is detected based on the morphological evolution. Mainly one phase MSi_2 is considered to show a diffusion pattern. We have found that the relative mobilities, measured by the ratio of the Si to metal tracer diffusion coefficients, decrease with an increasing atomic number in the given group. If determined at the same homologous temperature, the interdiffusion coefficients increase with the atomic number of the refractory metal in the MSi_2 phases. This behavior features the basic changes in the defect concentrations on different sublattices with a change in the atomic number of the refractory components.

Asymmetric ionic transport through the nanochannel

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Ionic channels are biological “nano-smart-machines” that control transport between the cell interior and exterior. Recently, the artificial nanochannels that mimic the functions of biological ion channels have attracted attention due to their potential applications in biosensors, medical implants and biomembranes. Designing such nanochannels that are selective and work without direct input of energy requires deep understanding and conceptualization of the dynamics of ionic transport.

Despite much research the mechanistic understanding of the transport and the selectivity of the molecular channels is still lacking. In this work the “magic” mechanism of the asymmetric ion transport through the molecular channels and related bio-mimetic devices is studied. The model is presented which provides a general physical mechanism for selectivity and high conductance of ionic channels and allows simulating the ionic transport through the cylindrical locally charged channel.

The model bases on the solution of the 3D Nernst-Planck-Poisson system for cylindrical geometry. The total flux includes drift (convection) and diffusion terms. Various initial conditions (channel charging and dimensions) are considered as the key parameters controlling the selectivity of the channel. The model allows determining the flow characteristic, calculating the local concentration and potential across the channel.

Study of ^{63}Ni grain boundary diffusion in SPD processed Cu-0.7%Cr-0.9%Hf alloy

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Quenched Cu-0.7%Cr-0.9%Hf alloy was processed by equal channel angular pressing (ECAP) and high pressure torsion (HPT). The microstructures of the samples were studied using EBSD immediately after HPT, ECAP and after subsequent annealing. In previous work it has been shown that the microhardness and the thermal stability of the severely deformed Cu-0.7%Cr-0.9%Hf alloy microstructure increase, while the average grain size decreases in comparison with pure deformed copper. The largest dislocation density is achieved by quenching and HPT in Hf-containing samples. Cu_5Hf phase precipitations are more effective in retarding grain growth in comparison with Cr particles and lead to additional hardening during aging.

Grain boundary (GB) diffusion in HPT and ECAP processed Cu-0.7%Cr-0.9%Hf alloy was measured in temperature interval between 150ºC and 300ºC by means of the radiotracer technique applying the ^{63}Ni isotope and utilizing precision grinding for sectioning. Profiles of ^{63}Ni in ECAP processed samples show percolating porosity and profiles in HPT processed samples don't. The GB diffusion coefficients correlate with GB diffusion in SPD processed pure Cu and Zr alloyed Cu.

The results are discussed with respect of the relationship between GB diffusion, the mechanical properties, microstructure and presence and state of non-equilibrium GB.

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Atomistic simulation of diffusion in alloys using non-lattice Kinetic Monte Carlo methods

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Diffusion in crystalline alloys have become of great interest for predicting and understanding defect and composition evolution at the nanoscale in materials used in microelectronics (such as SiGe alloys) or in nuclear energy applications (such as FeCr alloys). In this work, we present a comprehensive non-lattice Kinetic Monte Carlo model for defect diffusion and interdiffusion in crystalline binary alloys, and it has been specifically applied to SiGe and FeCr. The model is based on the properties of point defects and on the energy modifications of the system due to alloy mixing and strain. The microscopic parameters of the model have been linked analytically to macroscopic data on diffusion and phase-diagrams, and they have been calibrated in the whole composition range. The model has been implemented in the atomistic simulator MMonCa. For SiGe-based heterostructures, the model is able to reproduce the experimental interdiffusion data in a wide variety of conditions. On the other side, for FeCr alloys, which exhibit a region of spinodal decomposition, the model is able to predict the dynamics of diffusional transitions through the phase diagram during thermal aging, providing also interesting insights on the composition histogram evolution both for phase nucleation and spontaneous phase decomposition.

Simulation of atomic jumps with help of the constant temperature molecular dynamics method. New approach

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In our work we discuss the features of atomic jump simulation and associated problems. Then we present a new approach of the constant temperature molecular dynamics that fully takes into account the fluctuating character of this phenomenon. In addition the combination of molecular dynamics and molecular statics allowed within this model to take into account thermal expansion of the lattice and long-range elastic displacement of the atoms in the vicinity of defects. With the developed model, we study features of diffusion of carbon in iron. The analysis of a large number of diffusion jump trajectories allowed us to estimate the contribution of double jumps in the diffusion mobility. The diffusion mobility of carbon atoms at different temperatures was studied. We evaluated the influence of anharmonic effects on the diffusion mobility at high temperatures. Migration energy and pre-exponential factor are calculated. The temperature dependence of the migration volume is also determined. The isotope effect and its temperature dependence are calculated. We analyze the possible reasons for the acceleration of diffusion of carbon in α-iron at high temperatures.

Calculation of Kirkendall plane position in single and multiphase systems

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Kirkendall effect is well known phenomenon that proves the occurrence of vacancy mediated mechanism in diffusion processes in solids. However recent developments proved that this mechanism is by no mean simple. It was shown that bifurcation of Kirkendall plane occur in several multiphase systems. In this paper Kirkendall plane shift is simulated in Ni-Ti multiphase system and in ternary systems Co-Fe-Ni and Cu-Fe-Ni, where solid solution occurs. Kirkendall plane shift was estimated experimentally and by marker conservation method. This model allows to predict the Kirkendall plane positions not given experimentally. Explanation of this phenomenon is given. Experimental concentration profile was measured using Energy Dispersive X-ray Spectroscopy.

Modeling of a diffusive instability in electrochemical reactions

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In this talk we present a phase-field model for electrochemical reactions based on a grand canonical formalism. Similar to models for alloy solidification where the grand-canonical density writes in terms of the diffusion potential which is a variable that is same in both phases at equilibrium, in phase transformations coupled with charge transfer, the corresponding variable is the electrochemical potential which is a linear superposition of the diffusion potential and the electric potential. As a result, we derive the driving force for phase transformation as the difference of the grand-potential densities of the phases, which at leading order is proportional to the departure of the electrochemical potential from its equilibrium value. The equations of motion of the phase-field are solved in a coupled manner with the diffusion equation, which is governed by the gradient of the electrochemical potential, while the Poisson equation is satisfied at every point in the domain.

We present benchmark computations for the formation of the double-layer, the composition profiles and the profile of the electrical potential across a diffuse interface. In particular, we reproduce 'space-charge' regions in systems with local carrier densities, which form as a result of total depletion of carriers during equilibration. Thereafter, we apply the developed model to the problem of pore formation during etching of *p*-doped silicon in 2D. The etching reaction, at the interface of semiconductor and the electrolyte requires the transport of holes across a space-charge region in the semiconductor of low charge-carrier density. The width of the space-charge layer which is a solution of the Poisson equation is determined by the interface shape. Being directly proportional to the resistivity, the width of the space-charge influences the flux of holes appearing at the interface, thereby making the reaction front morphologically unstable. We reproduce this Mullins-Sekerka type instability in our phase-field simulations.

Radiotracer diffusion investigation of a structural phase transformation in near special Σ5 and Σ17 grain boundaries in Cu

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With the increasing fraction density of grain boundaries in fine- and ultrafine-grained materials, the effect of interfaces on material's properties becomes significant. The fundamental understanding of grain boundaries and their energy, structure and kinetics as a function of temperature and solute segregation is still incomplete. A promising method to gain the information about kinetics and structure is to use the radiotracer technique with individual, well characterized grain boundaries.

We will report the results of Ag diffusion in a Cu grain boundary of near Σ5(310)-type, in which a structural transition of the grain boundary was observed at approximately 850 K [1], which also appears in MD simulations [2]. The structure transition corresponded to both, a change of the effective activation enthalpy of diffusion and a disappearance of the diffusion anisotropy.

Further, a near Σ17(410) tilt grain boundary is investigated in the temperature range from 714 K to 1020 K. The grain boundary diffusion of ^{110m}Ag in this Cu bi-crystal is measured along the misorientation axis and the results are interpreted on the basis of MD simulations.

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Effect of Interface Phase Transformations on Diffusion and Segregation in High-Angle Grain Boundaries

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Recent experimental measurements of Ag impurity diffusion in the Σ5(310) grain boundary (GB) in Cu revealed an unusual non-Arrhenius behavior suggestive of a possible structural transformation Divinski et al., [Phys. Rev. B 85, 144104 (2012)]. We present atomistic simulations of Ag diffusion and segregation in two different structural phases of the Cu Σ5(310) GB which transform to each other with temperature. The obtained excellent agreement with the experimental data validates the hypothesis that the unusual diffusion behavior seen in the experiment was caused by a phase transformation. Together, the simulations and experiment provide convincing evidence for the existence of structural phase transformations in high-angle metallic GBs and demonstrate the possibility of their detection by GB diffusion measurements and atomistic simulations.

Grain boundary segregation of sulphur in nickel during annealing and during hot deformation

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Grain boundary (GB) segregation in nickel containing 5 wt ppm of sulphur in the bulk was studied by Auger spectroscopy and WDS after equilibration annealing at different temperatures. A segregation free enthalpy of -94 kJ/mol and a GB saturation concentration of 0.97 monolayer (= 66 ng/cm²) of sulphur were determined. The kinetics of segregation during annealing at 550°C and 750°C are consistent with the McLean equation and the sulphur bulk diffusivity of Vladimirov: it takes 2 months of annealing at 550°C to achieve equilibrium, whereas only 3 hours are enough at 750°C.

GB segregation during hot-compression was investigated as well. It was observed that at a given temperature of deformation, the sulphur GB concentration reaches the same equilibrium level as during simple annealing at the same temperature. However the kinetics of segregation during hot-deformation is faster by several orders of magnitude (1000 to 100000 depending on the deformation conditions). The other striking results are that the segregation kinetics during hot-deformation is linear upon time and proportional to the deformation rate. In addition, it is almost temperature-independent (in the temperature range investigated here). Models based on the acceleration of sulphur diffusion by supersaturated vacancies and moving dislocations are proposed.

Selenium redistribution after implantation in Germanium

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The continuous down scaling of microelectronic devices progressively leads to the silicon (Si) physical limitations, such as for the Si oxide that has already been replaced by high-k dielectrics in current transistor production. Germanium (Ge) is another important group IV semiconductor, presenting higher charge carrier mobility and smaller band gap. This material could conveniently replace Si in the CMOS technology. However, the common N-type dopants used in silicon technology, such as P and As, do not allow the fabrication of high doping levels in Ge due to their high diffusivity and their low solubility. Selenium (Se) is an N-type dopant from the column VI of the periodic table that has been poorly studied in Ge. In the present work, an Ge(001) substrate was implanted with Se atoms before to be annealed under vacuum. The Se redistribution was investigated by secondary ion mass spectrometry (SIMS), atom probe tomography (APT), and transmission electron microscopy (TEM). Despite a Gaussian initial distribution with a maximum located at a depth of ~ 60 nm, the Se redistribution profiles obtained after annealing are complex, exhibiting several maximums. APT observations show the formation of Se-Ge clusters of various compositions and sizes, distributed in a depth greater than 100 nm.

Short Range Atomic Movements in Amorphous Silicon Studied by Neutron Reflectometry

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Amorphous silicon (a-Si) is a model system of a covalent amorphous semiconductor, widely used in solar cells, flat screen displays and as a promising electrode material in Li-ion batteries. Yet, there exist no experimental data on self-diffusion in the amorphous state. The expected low diffusivities and intrinsic metastability of a-Si require the measurement of diffusion lengths of 1 nm and below as can be achieved by time-of-flight neutron reflectometry. ^{29}Si/^{28}Si isotope multilayers are prepared by ion beam sputtering and thermally treated in Ar atmosphere at temperatures below the crystallisation temperature in order to induce isotope interdiffusion. The amorphous nature of the films was shown by TEM and XRD. An onset of short range atomic diffusion on the length scale of 1 – 2 nm is found at about 350°C. Between 400°C and 500°C time-dependent diffusivities are found, which are interpreted as a consequence of structural relaxation. In contrast, additional experiments by Secondary Ion Mass Spectrometry indicate the absence of long range atomic motion in this temperature range. Different models for the explanation of the data are proposed.

The diffusing species in Ni silicide formation and its relation to relaxation mechanism

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The Ni-based self-aligned silicide is widely used as contacts and interconnections in very large-scale integrated circuits. It is obtained by solid state reaction between a Ni thin film and a Si substrate. NiSi is the desired phase in the Ni silicides as contact material in advanced integrated circuits. Therefore, the fundamental mechanisms related to their formation, such as knowing the phase formation sequence, identifying the fastest diffusing species and studying the phase morphology stability especially for NiSi, are of great interest for applications.

In this work, Ge was used as a marker to study the diffusing species during Ni silicide formation. 1 nm of Ge was deposited between 30 nm Ni film and Si substrate by magnetron sputtering. First, in-situ XRD measurements were performed to show that the formation sequence of Ni silicide phases is not affected by the presence of Ge. Atom probe tomography was used to reveal Ge atoms distribution in Ni silicides. The results obtained by APT show that Ni is the fastest diffusing element in the mixture layer formed during deposition as well as in δ-Ni2Si, and in NiSi phases that form during heat treatment. Moreover, APT analysis before and after relaxation of the δ-Ni2Si phase bring more insights on the stress relaxation mechanism.

Capillary phenomena in thin films: When interface diffusion becomes dominant

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We demonstrate the important role of metal self-diffusion along the metal-substrate interface in capillary phenomena in thin metal films deposited on ceramic substrates.

(1) Ni films, 40 nm thick, were deposited on sapphire substrates. The films were polycrystalline, with a strong in- and out-of plane texture. Grains in the film, ~200-800 nm in size, were arranged as a mazed bicrystal. Thermal grain boundary grooving in the films was studied at 700°C. The observed groove shape deviated substantially from Mullin's classical solution, and showed an apparent negative mass balance. We proposed a model which explains this by considering Ni self-diffusion along the film-substrate interface and homogeneous thickening of the film. The new, closed solution was in good agreement with experimental results.

(2) Fe films, 3 nm thick, were deposited on sapphire substrates. Annealing at 1100°C resulted in dewetting of the film and formation of Fe nanoparticles. With increasing annealing time, the number of particles decreased and isolated Fe nanowires formed at their expense. To explain this counter-intuitive phenomenon, we proposed a model which considers Fe self-diffusion from adjacent nanoparticles to the nanowire-substrate interface as the main growth mechanism. The obtained growth law was in good agreement with experimental results.

Grain boundary diffusion of Si in Cu

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In this work we are reporting our recent experiments on measuring the grain boundary (GB) and triple junction (TJ) diffusion of Si in sputter deposited Cu. Two main methods have been used. Surface accumulation tests by x-ray photoelectron spectrometry (XPS) and low energy ion scattering (LEIS) provided an averaged diffusion coefficient for the whole shortcut system, while atom probe tomography (APT) allowed the characterization of the individual defects.

APT measurements indicated a C-A type diffusion (according to the characterization of Divinski et. al [1]), i.e. the diffusion is restricted to the GB-s (C-type), but the diffusion fields of the individual TJs are completely overlapping. TJ diffusion is about 100 times faster than GB diffusion (10^{-19} m^2s^{-1} and 10^{-21} m^2s^{-1}, respectively). XPS-LEIS measurements at the same temperature have provided a averaged GB diffusion coefficient closer to the TJ diffusion coefficient. Consequently for an accurate description of the diffusion in nanoscale materials more complex models, taking the TJ diffusion into account have to be used [2].

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Hydrogen impurity in tin dioxide

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Tin dioxide (SnO_2) is one of the very useful oxide semiconductor and has been utilized as chemical sensors and transparent electrodes. It has been considered that its native n-type conductivity is originated in its non-stoichiometry. However, recent investigation of oxide semiconductors using density functional theory indicated that native point defects in SnO_2 should not be the origins of its native conductivity. In order to explain the inconsistency between observed n-type conductivity and theoretical predictions, the theory suggested that the hidden donor in SnO_2 is hydrogen. With those background, we are motivated to investigate hydrogen behavior in SnO_2 in search for the hidden donor in SnO_2 [1, 2]. We employed thermal treatment in humid atmosphere for intentional hydrogen doping into SnO_2 and, in particular, we employed heavy water for those treatment to enable us isotope tracer study. As a result, we realized that there are at least two kinds of hydrogen sites in SnO_2 in terms of migration behavior. We will discuss the hydrogen sites in SnO_2 using the results of total energy calculation for SnO_2 doped with hydrogen.

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Phosphorus diffusion and incorporation in silicon nanoclusters embedded in silicon oxide

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The interest towards deterministic doping of semiconductor nanostructures has increased over the last decade. However, no clear understanding is still reached as the mechanisms of doping at nanoscale are significantly different from those in bulk materials and also because of extremely challenging characterization issues.

We considered the doping of 4 nm Si nanoclusters (NCs) embedded in SiO_2 by diffusion of phosphorous from a solid source 20 nm far away. In our experiment, P diffusion and segregation at NCs occurs after the NC formation, allowing their investigation without the interference of phase transitions, as a function of annealing times and temperatures. The dopant concentration profile have been characterized by ToF-SIMS and RBS and have been fitted by a rate equation model able to reproduce P diffusion in oxide and P capture and release by NCs, extracting the associated thermal energy barriers. The results have been related to the NCs size, arrangement, crystal phase and thermal stability obtained by TEM analysis and to the P chemical surrounding obtained by XPS.

This fundamental approach on a well assessed template system, provided valuable insights on the Si nanoscale doping and in principle could be also applied to investigate other nanostructures.

Early stages of the Cu3Si phase growth: combination of SNMS, XPS, XRD, and APT techniques

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The Cu_3Si phase holds a great technical interest in the fields of solar cells, power sources or optical data storage. Hereby we report our results about the growth of this technically important phase of the Cu–a-Si system. Using multiple complementary tools (SNMS, XPS, XRD, APT and 4 wire resistance) we found a rapid nucleation of a ~20 nm thick silicide phase which one was followed by a much more slower growth. By the above mentioned techniques we demonstrate that the growth of the Cu_3Si crystalline layer at 408K between the amorphous Si and nanocrystalline Cu thin films follows a linear law and the shifts of the two interface of the Cu_3Si phase approximately equally contributed to the full growth of this phase. It is also illustrated that the Si atoms diffuse fast into the grain boundaries of the nanocrystalline Cu, leading to Si segregation on the outer surface. The APT and SNMS results indicate that even already during the deposition of Cu on the amorphous Si an intermixed region is formed at the interface. This easily transforms subsequently into a homogeneous Cu_3Si crystalline reaction layer which further grows following apparently an interface controlled linear kinetics.

Mass Transfer along Grain Boundaries in Polycrystalline Alumina under Oxygen and Water Vapor Potential Gradients at High Temperatures

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The durability of thermal barrier coatings is strongly affected by mass transfer along grain boundaries (GBs) in alumina scales formed on the bond coat. We previously evaluated the oxygen permeability of polycrystalline alumina wafers, which serve as models for the alumina scales, for a large oxygen potential gradient at high temperatures. The dependence of the oxygen GB diffusion coefficient on the oxygen partial pressure (P_{O_2}) was first determined for small oxygen potential gradients associated with a combination of low P_{O_2} values. In this case, oxygen permeation occurred mainly by GB diffusion from the high P_{O_2} surface to the low P_{O_2} surface. The oxygen GB diffusion coefficient through the wafer for large oxygen potential gradients, where oxygen and aluminum interdiffuse, was then predicted by extrapolation to higher P_{O_2} values.

In the present study, alumina wafers were exposed to a large oxygen potential gradient at a temperature of 1873 K, with $^{18}O_2$ being included as a tracer. The GB diffusion coefficient for oxygen near the high P_{O_2} surface were then experimentally evaluated based on the ^{18}O depth profile determined by secondary ion mass spectroscopy, and compared with the values predicted by extrapolation. Furthermore, the effect of water vapor on oxygen GB diffusivity was evaluated using both $^{18}O_2$ and D_2O tracers.

Retardation of grain boundary diffusion under the action of the surface tension gradient

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Based on recently obtained experimental data for Fe and Co diffusion in Cu, the question is discussed on the reasons of the absence of accelerated grain boundary diffusion (GBD). Contrary to the classical treatment, in frame of Fisher-Gibbs model, the new model was developed taking into account two driving forces – the concentration gradient and connected gradient of grain boundary (GB) surface tension (excess free energy of GB). Few cases were discussed, including:

- positive and negative adsorption of diffusant;
- GBD in "B" and "C" regimes.

It is shown that in the case of positive adsorption the effect of the additive driving force (surface tension gradient) is negligible, but the effect is of considerable importance in the case of sufficiently large negative adsorption (the enrichment coefficient of GB adsorption $s < 0.3$) and sufficiently large values of diffusant concentration.

As for temperature dependence, it is important to note, that in the case of positive adsorption the segregation energy is negative, whereas GBD activation energy (under the action of concentration gradient) is positive. Meanwhile, in the case of negative adsorption both energies are positive. Thus, GBD decreases faster than in classical situation.

Thermal conductivity of isotopically enriched silicon nanostructures

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The concept of reducing thermal conductivity without degrading the electrical conductivity is most ideally realized by controlled isotope doping: the thermal conductivity of Si can be effectively reduced by means of isotopic nanostructuring [1,2] and make this engineered material suitable for thermoelectric devices. In this work we report measurements on the thermal conductivity of periodic and aperiodic alternating layers of Si enriched with different stable isotopes and grown epitaxially on (100)-oriented natural Si substrates. Thermal conductivity in the cross plane direction was measured with time-resolved X-ray scattering at the European Synchrotron Radiation Facility (ESRF). For these measurements the isotope structures were covered with a 30 nm thick gold film. The cooling of the Au layer after pulse-heating with a femtosecond laser was followed by measuring the lattice constant with X-ray. The effective thermal conductivity of the isotopically modulated multilayer is determined from numerical simulations of the heat transport problem. Measurements were also conducted by means of the three omega measurement method.

Different isotopically enriched silicon nanostructures were investigated in order to determine the effect of the layer ordering, the number of layers, the broadening at the layer interfaces, and of the lateral confinement on thermal conductivity.

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Modelling of physical properties of functional gradient thermoelectric materials

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The numerical model describing the effects of gradients of physical properties (i.e. carrier concentration n, Seebeck coefficient, electrical conductivity, and thermal conductivity) on the energy conversion efficiency of a functionally graded thermoelectric material (FGTM) has been presented. The model allows calculations of temperature distribution in the FGTM and the efficiency as a function of current density for given profiles of carrier concentration. It was confirmed that a maximal value of figure of merit ZT_{max}, as a function of carrier concentration, is attained just for one specific location of the Fermi level, with respect to the conduction band edge. The developed model allows calculation of optimal dopant concentration profile especially in FGTM element prepared by high-gravity sedimentation method.

Impact of *p*-type doping in self- and dopant diffusion in Germanium

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Simultaneous experiments on self- and *n*-type dopant diffusion in germanium (Ge) isotope multilayer structures reveal that doubly negatively charged vacancies mediate self-diffusion under intrinsic and *n*-type doping conditions [1,2]. To determine the preferred charge state of the Ge vacancy under *p*-type doping, the Ge self-diffusion under boron (B) doping is investigated by means of homogeneous B doped Ge isotope heterostructures grown by molecular beam epitaxy (MBE). Electrical and chemical profiling of the isotope structure by use of spreading resistance and secondary ion mass spectrometry, respectively, confirm full activation of B. Diffusion experiments performed with these B-doped isotope structures at temperatures between 800 K and 1020 K clearly indicate a reduced self-diffusion under *p*-type doping compared to electronically intrinsic conditions. This not only confirms the acceptor nature of vacancies in Ge but also provides information about the energy levels introduced by the vacancy in the band gap of Ge.

Furthermore B diffusion under gallium (Ga) doping in Ge is investigated. Whereas B diffusion in silicon is clearly mediated by self-interstitials, the impact of self-interstitials on B diffusion in Ge is only observable under non-equilibrium conditions established e.g. via irradiation [3,4]. To examine the mechanism of B diffusion in Ge under thermal equilibrium we performed simultaneous experiments on B and Ga diffusion. These experiments will reveal the diffusion behavior of B under extrinsic *p*-type doping.

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Triple junction transport and the impact of grain boundary width in nanocrystalline Cu

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Triple junctions, are singular topological defects of the grain boundary structure, which can get a dominant role for grain growth and atomic transport in nanocrystalline matter. In this work the atomic transport along triple junctions and grain boundaries has been studied using the three dimensional atom probe tomography technique in the nanocrystalline Ni-Cu system. In the completely miscible alloy system, we could demonstrate that in the triple junctions of nanocrystalline Cu the diffusivity of Ni is 100-300 times higher than in related high angle grain boundaries. The measurements also revealed that the chemical (or segregation) width of grain boundaries unexpectedly varies with temperature. This segregation layer at the grain boundaries grows from 0.7 nm at 563 K to 2.5 nm at 643 K. This variation is not controlled by simple volume diffusion. Furthermore, it was proven by kinetic analysis that the effective transport width has to possess a significant dependence on temperature. The transport product of triple junction diffusivity has been accurately measured as a function of temperature. If the variation in grain boundary width is taken into account, the activation energies for Ni diffusion in triple junctions and grain boundaries in Cu can be determined to be 83±10 and 120±15 kJ/mol, respectively. Accordingly, triple junctions represent a significantly faster diffusion route and are also characterized by lower activation energy than grain boundaries.

Evolution of tilt grain boundaries during interstitial segregation

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Nowadays various models of radiation-induced evolution of nuclear reactor's structural materials and nuclear fuel's components are used. In this models, grain boundaries (GB) and dislocation network are presumed to be unsaturable sinks. This assumption is known to be appropriate at temperatures close to the melting point of material, when GB amorphisation and premelting occurs.

However, for the temperatures of nuclear reactor's operation, applicability of this approach was insufficiently proved. It was not clear how the segregation of defects influences various properties of grain boundaries. Whether the grain boundary can be saturated as a sink of point defects or not.

In this work we used molybdenum bicrystal as an object of investigation. By the means of classical and accelerated molecular dynamics we studied evolution of grain boundary formation energy and structure during interstitial segregation. Several tilt GB in a wide range of misorientation angles were considered. The basic regimes of defect-GB interaction were determined. The results of conducted atomistic modeling revealed that some types of grain boundaries are able to recover their structure after segregation certain number of defects. The results obtained in this work affirm the assumption that GB sink strength for point defects does not saturate.

Molecular Dynamics Simulations of Ternary Polymer Electrolyte-Ionic Liquid Mixtures

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Electrolytes based on mixtures of lithium salts and poly(ethylene oxide) (PEO) are important candidates for modern lithium ion batteries. Unfortunately, in case of the common binary electrolytes like PEO/LiTFSI, the ionic conductivity is still too low for an efficient technological use. Here, the incorporation of an ionic liquid (IL) into these materials promises a significant improvement, as the conductivity is increased about an order of magnitude at room temperature.

Motivated by these experimental findings, we study the underlying microscopic transport mechanisms of the lithium ions by means of Molecular Dynamics simulations. Essentially, we find that these mechanisms are qualitatively the same as in binary PEO/LiTFSI for most electrolyte compositions, and that the overall lithium transport can be described by a Rouse-based analytical ion transport model. When adding the IL into the electrolyte, the characteristic time scale of one of the mechanisms, namely the cooperative motion with the PEO segments, is reduced significantly [1]. From a practical perspective, however, it turns out that this enhancement is only observed for sufficiently low lithium concentrations, for which the PEO segments remain mobile enough [2].

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Molecular Dynamics Study of the Heat of Transport in a Liquid NiAl Alloy

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We analyse the formalism of thermotransport in a binary system especially focussing on a detailed consideration of the heat of transport parameter characterizing diffusion driven by a temperature gradient. We introduce the reduced heat of transport $Q_c^{*'}$ which describes part of the interdiffusion flux that is proportional to the temperature gradient. In an isothermal system $Q_c^{*'}$ represents the reduced heat flow (pure heat conduction) consequent upon unit interdiffusion flux. We demonstrate that $Q_c^{*'}$ is independent of reference frame and is practically useful for direct comparison of simulation and experimental data from different sources obtained in different reference frames. Then, we use equilibrium molecular dynamics simulations in conjunction with the Green-Kubo formalism to study the heat transport properties of a model of a liquid $Ni_{50}Al_{50}$ alloy at three state points within the temperature range 1500 – 4000 K. Our results predict that in the liquid $Ni_{50}Al_{50}$ alloy in the presence of a temperature gradient Ni tends to diffuse from the cold end to the hot end whilst Al tends to diffuse from the hot end to the cold end.

Interaction between vacancies and interstitial solutes (C, N and O) in α -Fe: thermodynamic and kinetic consequences

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Carbon, nitrogen and oxygen atoms are always present in α-Fe, either as impurities or as alloying elements. We show that, despite low solute concentrations and even lower equilibrium vacancy concentrations, vacancy-solute clusters are non-negligible and lead to a lowering of vacancy formation energies in Fe and an increase of solute solubility limits. Under irradiation conditions, these clusters result in radiation induced segregation phenomena.

A generalized Hamiltonian is derived on the perfect body-centered cubic lattice including substitutional and octahedral interstitial sites. Interactions are fitted to a whole set of Density-Functional Theory calculations of vacancy-solute clusters binding energies. The atomic diffusion model parameters are fitted to vacancy and solute migration barriers in various environments.

Using the Hamiltonian, vacancy formation energies and solute solubility limits are obtained from Low Temperature Expansions (LTE). The Self-Consistent Mean Field (SCMF) formalism is extended to systems containing two migrating species located on two sublattices. The atomic diffusion model is inserted into the SCMF formalism and LTEs are used to calculate the ensemble averages and the resulting full Onsager matrix of the system. The amplitude and sign of flux couplings, as well as cluster mobilities, are deduced from these Onsager coefficients.

Grain boundary diffusion of Ti and Ni in B2 NiTi compound

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The radiotracer technique was used to measure the grain boundary diffusion of ^{44}Ti and ^{63}Ni in slightly Ti-rich polycrystalline NiTi compound in the temperature range of 673 - 923 K. The temperature dependence of the grain boundary triple product P ($P = s\delta D_{gb}$, s is the segregation coefficient, δ is the grain boundary width, and D_{gb} is the grain boundary diffusion coefficient) for Ti and Ni was determined and compared with the literature data measured for other B2-ordered alloys. Although the grain boundary diffusion rates show similar orders of magnitude when plotted against the inverse temperature normalized on the melting point of the corresponding compounds, the temperature dependencies of both Ti and Ni grain boundary diffusion in NiTi reveal a unique behavior with significant deviations from an Arrhenius-type dependence. Possible diffusion mechanisms and grain boundary structures were used to interpret this phenomenon.

Vacancy Mediated Cation Migration in Uranium Dioxide; the Influence of Cluster Configuration

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The migration of uranium in uranium dioxide is an important factor in determining the mobility and release of fission gases from fuel pellets, as well as being a key parameter in the recovery from radiation damage. The effect of cluster configuration on vacancy mediated uranium migration is investigated for stoichiometric UO_2 and hyper-stoichiometric UO_{2+x} using atomistic simulation. It has been shown that the minimum enthalpy pathway involves reconfiguration of the most stable charge neutral cluster to a metastable configuration, in stoichiometric and hyper-stoichiometric systems. The reduction in migration enthalpy due to cluster rearrangement was 0.19 eV in UO_2 and 0.64 eV in UO_{2+x}. Additionally, a much larger number of alternative metastable configurations were identified for UO_{2+x} compared to UO_2. As such, a large contribution to the Arrhenius pre-exponential term with hyper-stoichiometry is expected. This effect is expected to be the case for many other systems where clustering occurs and we expect this to be just the first example of a common issue.

Multiscale, Multiphysics Modeling/Simulation based on Ultra-Accelerated Quantum Chemical Molecular Dynamics for Complex Diffusion Processes of Industrial Importance

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Much attention has been given to diffusion processes in a variety of industrially important systems such as Li-ion battery, fuel cells, and electronic devices. In collaboration with many experimental/industrial experts, the authors have developed multiscale, multiphysics simulators for the design of such batteries and devices. The objectives of the present study are to confirm the accuracy and applicability of these simulators for complex diffusion processes in industrially important systems. In our previous studies UA-QCMD method with the first-principles parameterization is 10,000,000 times faster than the conventional first principles molecular dynamics method.

In the present study we demonstrated that the quantum chemical calculation in UA-QCMD has high accuracy in comparison with DFT and thermodynamic data. It was also demonstrated that the UA-QCMD method is effective in calculating the local physico-chemical properties necessary for mesoscopic and macroscopic simulations. The multiscale, multiphysics simulators based on UA-QCMD method were developed and demonstrated to be quite efficient for calculating the complex diffusion processes in batteries for automotive applications. It was also demonstrated that the multiscale, multiphysics simulators are useful for investigating detailed mechanism of electromigration in metallic interconnects of electronic devices.

Quantifying the vacancy concentration gradient adjacent to interfaces exposed to irradiative fluxes

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The efficacy of interfaces as sinks for point defects will impact the non-equilibrium point defect concentration in materials exposed to an irradiative flux. Quantifying the relative rates at which Frankel pairs annihilate via mutual recombination or at interfaces, and relating this to the efficacy of the sink has been experimentally challenging. We have employed local chemical tracer diffusivity measurements performed as a function of distance from an interface to calculate the local non-equilibrium vacancy concentration. Broadening of the chemical tracer is quantified via energy dispersive spectroscopy performed in a scanning transmission electron microscope. This information may be used to reconstruct the vacancy concentration gradient adjacent to the interface, provide insights into the relative rates of mutual recombination and annihilation at interfacial sinks, and serve as an approach to quantifying the efficacy of the interfacial sink. This work specifically investigates different interfaces (e.g. Cu-Nb, Cu-V, and Cu-Ni) as sinks for non-equilibrium point defects.

Effects of compression tests on point defects in pure Ni and Ni-16 at.% Cr model alloys

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In the context of nickel-based superalloys for the next GEN4 nuclear powerplant, the effect of compression tests on point-defect concentrations and dislocations in pure Ni and Ni-16 at. % Cr model alloys is studied. Point-defects and dislocations concentrations are respectively characterized by positron annihilation spectroscopy and x-ray diffraction analysis. In support to the experimental work, atomic based kinetic models are used to characterize point-defect – dislocation interactions and to estimate the evolution of the vacancy concentration during annealing treatments.The first results obtained for 30 % and 60 % compression tests shows that only mono-vacancies are formed with concentrations higher than the equilibrium values. A slightly lower vacancy concentration is observed in the alloy due to its finest microstructure where grain-boundaries potentially act as vacancies sinks.

The saturation of defects concentration measured by X-ray and positrons seems to appear under the value of the realized deformation rate. The evolution of the vacancy concentration during the annealing treatment of samples is predicted by a kinetic model taking into account the variation of vacancy formation and migration energy with the alloy composition and the interaction between vacancy and dislocations. It is then planned to compare these predictions with experiments.

Kinetic of Void Growth in Cubic Metals. Theory and Simulation

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We examine how elastic stress, arising from nanovoids influence the diffusion vacancy fluxes using new approach. Our approach takes into account, that strain values are different in the saddle point and in the rest atom position, in differ from our earlier works. One of the chief aims of our work is to obtain a kinetic equation for the growth rate of voids in cubic metals. In using diffusion equations, the functional dependence on strain is determined by coefficients, which are the main characteristics of the strain influence on diffusion (SID coefficients). These coefficients are very sensitive to atomic structure in the nearest vicinity of the saddle-point configuration. We have built advanced model to evaluate them. SID coefficient simulation is the first step of this work. Then the diffusion equation for vacancies in which the influence of elastic stress near the void on flux was taken into account is linearized and resolved. The obtained kinetic equation for the growth rate of voids contains the additional terms conditioned by strains. This feature distinguishes the equation from ones that are known and changes the kinetic of void growth. Using the kinetic equation, we simulate void growth in cubic metals under different conditions.

Interdiffusion in liquid Al-Ni alloys studied by time-resolved X-ray radiography

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The relation of self- and interdiffusion is controlled by thermodynamic driving forces and kinetic influences described by the thermodynamic factor Φ and a measure of cross correlations S (called Manning factor in crystals). For low concentrations Φ and S are expected to approach unity. In Al-Ni the thermodynamic factor Φ calculated from Gibbs free energy data [1] is below unity for Ni-concentrations of less than 7 at%. This behaviour is not seen in molecular dynamic simulations where Φ is always larger than unity.

We report on the experimental investigation of interdiffusion in aluminium-rich Al-Ni melts employing X-ray radiography. X-ray radiography allows for time-resolved in situ observation of the diffusion process. It is combined with the shear cell technique to avoid influence of flow effects during melting of the diffusion couple. Experiments were carried out aboard the sounding rocket MAPHEUS, to avoid gravity driven flow, as well as on ground.

Data are compared to results of self-diffusion coefficients obtained by quasielastic neutron scattering as well as to molecular-dynamics computer simulations. We discuss the influence of the thermodynamic factor and show that Darken's approach does not give a sufficient description.

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Component Diffusivities Decoupling in Glass Forming Zr-based Melts

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Metallic alloys can transform into a glassy state, when cooled rapidly enough to avoid crystallization. Structure and dynamics - in particular diffusion and viscosity - in the melt of an alloy determine the glass forming ability. Previously [1], we have shown that above the critical temperature T_c of Mode Coupling Theory and in the equilibrium melt, diffusivity of the majority component Pd and of the smaller components in glass forming Pd-Ni-Cu-P alloy merge to one diffusivity value (no decoupling). Here, we extended our investigation to glass forming Zr-based melts. We report ^{95}Zr and ^{57}Co radiotracer diffusivities in the equilibrium liquid state of a bulk metallic glass forming Zr-Ti-Cu-Ni-Be [2] and in binary Zr-Ni melts far above the liquidus temperature T_l. The results are not affected by convection as evidenced via quasi-elastic neutron scattering. In contrast to Pd-based alloy, the majority component Zr diffusivity is strongly decoupled from diffusivity of the smaller components above T_l by at least a factor of four although it still obeys the Stokes-Einstein equation. The results suggest that in metallic glass forming Zr-based alloys, diffusion and viscous flow start to develop solid-like, i.e. energy-landscape controlled, features already in the stable liquid state far above the mode coupling T_c.

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Study of oxygen diffusion paths in $BaTiO_3$ ceramics doped with Ho

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Barium titanate ($BaTiO_3$) is one of the most important compounds used in the electroceramic field; it is used in multilayer ceramic capacitors (MLCCs) [1] and positive temperature coefficient resistors (PTCRs) [2]. Above devices usually have rare-earth elements (REEs) and other elements to control the microstructure, conductivity, and electrical degradation. Recent MLCCs and PTCRs have a multilayered structure of $Ni/BaTiO_3$ [3]. This structure needs to co-fire Ni and $BaTiO_3$ in a reducing atmosphere. So, we fabricated the semiconductive $BaTiO_3$, and studied on the hydrogen incorporation and oxygen diffusion paths [4].

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Diffusion of oxygen in amorphous oxides

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Amorphous oxides such as Al_2O_3 (a-Al_2O_3), a-Ta_2O_5, and a-Nb_2O_5 have unique structural properties; the difference in density between the amorphous and the counter-part oxides is up to 40%, indicating that they contain large amount of atomic-level spaces. By using such defective structures, nanoporous structures have been found to form as a result of structural change and crystallization through annealing. As pointed out in previous works, void formation is related closely to the changes in amorphous structure towards crystallization; structural change initiates nanopore formation before crystallization and further growth of nanopores occurs by crystallization. In order to expand nanoporous oxides prepared by the technique in potential applications as functional materials for ion exchange, molecular separation, catalysis, chromatography, and microelectronics, more knowledge is needed about how to control the size and density of nanovoids. For the purposes, both structural and kinetic aspects of the amorphous oxides should be well understood. However, knowledge on their diffusion properties is quite limited. In the present work, diffusivity of the common element, oxygen, in amorphous a-Al_2O_3, a-Ta_2O_5, and a-Nb_2O_5 has been investigated. We discuss the diffusion properties of amorphous oxides, considering the short-range atomic structures.

Oxygen and Calcium Diffusion in Mayenite

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The structure of Mayenite ($Ca_{12}Al_{14}O_{33}$) can be described as a positively charged $(Ca_{12}Al_{14}O_{32})^{2+}$ framework, consisting of six cages of which 1/6 are occupied with the remaining oxygen ion. This “free” oxygen ion possesses a high mobility. At $T > 573$ K, Mayenite exhibits an oxide-ion conductivity, similar in magnitude to YSZ [1].

In this study we investigated oxygen and calcium diffusion in Mayenite crystals by $^{18}O/^{16}O$ and $^{42}Ca/^{40}Ca$ isotope exchange experiments, and we analysed the diffusion profiles in the samples by means of Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

Oxygen tracer diffusion coefficients D^*_O and surface exchange coefficients k^*_O were determined as a function of temperature ($773 \text{ K} < T < 1273 \text{ K}$) at an oxygen activity of $a_{O_2} = 0.1$, as well as a function of oxygen activity ($0.01 < a_{O_2} < 0.9$) at $T = 1123$ K. The measurements reveal two independent diffusion processes, which are attributed to the diffusion of different “free” oxygen species.

Calcium tracer diffusion coefficients D^*_{Ca} were determined in air as a function of temperature ($973 \text{ K} < T < 1273 \text{ K}$) and as a function of oxygen activity. The diffusion coefficients are several orders of magnitude lower than for those of oxygen but surprisingly high, given that calcium constitutes part of the cage framework.

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Diffusion in shear bands of a $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass

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Bulk metallic glasses have received increasing attention due to their advanced properties which are auspicious for many fields of application. Besides their high corrosion-resistance, metallic glasses exhibit high strength and hardness. Nevertheless, the promising mechanical properties are disadvantaged by the extremely limited plastic deformation. Throughout deformation, the plastic strain localizes in thin regions of the widths of 10 nm to 50 nm, the so-called shear bands. The formation of shear bands is the reason for subsequent catastrophic failure. Despite their obvious importance, there exist several open issues concerning the initiation, propagation, kinetics and general understanding of shear banding.

In the present study, the characteristics of shear bands in a $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass are investigated more precisely utilizing the radiotracer technique to measure the rate of atomic transport within the shear bands. The plastic deformation is performed by controlled rolling in one step to different strains at room temperature. The combination of these experimental results with calorimetric measurements gives further insight into the impact of structural changes on diffusion.

Diffusion in glass forming metallic melts

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When cooled rapidly enough to avoid crystallization, even metallic alloys can transform into a glassy state. Structure and dynamics - in particular diffusion and viscosity - in the melt of an alloy determine the glass forming ability. While the diffusion mechanism in the glassy state is well known [1], it is still not clear, how the components in these alloys diffuse and how diffusion and viscosity are related. We report radiotracer diffusivities in Pd- and Zr-based melts, presenting for the first time a complete set of data for all components over the whole relevant temperature range from the glassy state to the equilibrium melt. While a vast decoupling of more than 4 orders of magnitude is observed between the diffusivity of Pd and of the smaller components [2], at the glass transition temperature T_g, the diffusivities of all components merge close to the critical temperature T_c of mode coupling theory. For Pd, the Stokes-Einstein relation holds in the whole range investigated encompassing more than 14 orders of magnitude suggesting the formation of a slow subsystem as a key to glass formation [3]. In multicomponent Zr-based melts, diffusivities are even decoupled in the equilibrium melt far above T_c [4].

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Diffusion, Structure and Crystallization in a HPT-deformed bulk metallic glass

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Metallic glasses show unique properties compared to their crystalline counterparts, but their applicability is limited by the lack of sufficient plasticity. Stress localization and the associated shear softening weaken strongly the structure, thus leading to the formation of shear bands. The structure of shear bands is still far from being understood. High pressure torsion (HPT) allows the deformation of metallic glasses towards very high strains without a shape change and thus without catastrophic failure of the material. The regions of shear localization, i.e., the shear bands, experience severe deformation conditions and the number density of such regions is maximized under HPT processing. Thus, severely deformed glasses can act as a model system for integral testing methods such as calorimetry or diffraction analysis. Due to their extreme sensitivity to the free volume localization, the diffusion measurements by the radiotracer technique can bring further insight into the structural modifications of shear bands with respect to the amorphous matrix as well as to the conditions of shearing during plastic straining. Here, the results of a combined study of the diffusion process, the crystallization behaviour and the structure evolution of a HPT-deformed Zr-based bulk metallic glass are reported.

Low-temperature alpha silver iodide confined in glass: structure and dynamics

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In 1937, W. Jost speculated about the possible positions and dynamics of the silver ions in the high-temperature phase of silver iodide, α–AgI, that one would encounter, if it could be cooled far below its regular 147 °C α–β phase transition. Would a (continuous) 'liquid-solid transition' occur in the silver sublattice and would the 'liquid-like' dynamics of the mobile silver ions change into a 'solid-like' hopping motion? We are now, for the first time, able to answer Jost's questions, both of them in the affirmative. In our samples, globules of crystalline α–AgI were contained in a powdered glass of composition $0.78\ \mathrm{AgI} \cdot 0.165\ \mathrm{Ag_2O} \cdot 0.055\ \mathrm{B_2O_3}$, prepared from the melt by roller quenching and subsequent grinding in liquid nitrogen. In a Rietveld refinement of x-ray diffraction data, taken at 100 K, the silver ions were found to be localized within the tetrahedral voids provided by the α–AgI anion structure. The change from the high-temperature 'liquid-like' dynamics of the silver ions into a 'solid-like' hopping motion could be verified by considering spectra of the ionic conductivity. With decreasing temperature, the spectra do, indeed, develop the characteristic frequency dependence which is a hallmark of ionic hopping.

Li+ ion diffusion in lithium niobate

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Ionic diffusion and conduction play an important role in the development of materials for energy conversion and storage. Determination of Li+ ion diffusion coefficients and diffusion mechanisms is still challenging and an essential prerequisite for screening fast Li+ ion conductors. Traditionally, ion diffusion coefficients are determined by measuring diffusion profiles, particularly with tracers. Spectroscopic methods such as NMR, impedance spectroscopy, etc., are also used to derive ionic diffusion coefficients. Here we present a unique technique to determine Li+ ion diffusion coefficients in lithium niobate single crystals by using optical in-situ spectroscopy at high temperatures. This uncommon method is particularly powerful for the study of defect chemistry and ion diffusion in oxides.

The intrinsic non-stoichiometry of lithium niobate produces lithium vacancies and anti-site niobium ions. Upon chemical reduction in atmospheres of low oxygen activity, the defect structure of lithium niobate is further enriched by generation of electron polarons

($\mathrm{Nb}_{\mathrm{Nb}}^{'}$) with the charge neutrality condition: $\mathrm{V}_{\mathrm{Li}}^{'} + \mathrm{Nb}_{\mathrm{Nb}}^{'} = 4\,\mathrm{Nb}_{\mathrm{Li}}^{\bullet\bullet\bullet\bullet}$. The optical absorption of electronic defects, e.g., electron polarons provides a probe to monitor oxidation and reduction processes induced by sudden changes in oxygen activity in the surrounding atmosphere of the sample. The time-dependent absorbance change can be analyzed using a diffusion model to derive chemical diffusion coefficients as well as those of defects and ions. For example, the Li+ ion diffusion coefficient in congruent lithium niobate is determined to be 6.8×10^{-13} m^2/s at 1000 °C with an activation energy of 1.43 eV.

Ion Transport in Solid Polyelectrolyte Materials

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Polyelectrolyte multilayers (PEM) and polyelectrolyte complexes (PEC) are interesting materials for application as ion conductors, as they can be prepared with defined thickness or defined stoichiometry, respectively [1,2]. Ac conductivity spectra characterize the ionic transport processes over many decades of frequency, providing a full picture of long-range transport as well as local motions. In temperature-dependent spectra of dry PEC, the time-temperature superposition principle (TTSP) is shown to be valid [3]. For spectra taken at different relative humidity (RH), a new scaling principle in analogy to TTSP, termed time-humidity superposition principle, is established. This model-free scaling holds for different materials over several decades in frequency [4]. The reason is that with increasing RH water is absorbed into the PEC which changes the energy landscape so that ion motions are strongly facilitated. Temperature-dependent spectra taken at constant water content yield additional information on hopping processes of ions in PEC.

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Tailoring of interfaces in amorphous silicon-germanium multilayers on the atomic scale by ultra-high gravity

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With decreasing characteristic length, density and relevance of interfaces, such as phase or grain boundaries, increase and may control the physical properties of nanostructured materials. The abruptness of the interface between different phases can be crucial for various technologies. Interface manipulation on the atomic scale may provide a useful tool for tuning electronic, magnetic and optical properties of multi-layered structures as used, for example, in X-ray and neutron mirrors, mirrors for extreme ultraviolet lithography, giant or tunnelling magnetic resistance devices, multi-quantum wells, electrical devices and other functional assemblies containing interfaces. After summarizing our previous results in the field of interface tailoring [e.g. Z. Erdélyi et al. PRL 89, 165901 (2002); Z. Erdélyi et al. Science 306, 1913 (2004), Z. Balogh et al. APL 99, 181902 (2011)], we will show our recent achievements: Amorphous Si/Ge multilayer containing diffuse interfaces have been prepared, heated in an ultra-centrifuge and subsequent interface structure modifications observed by X-ray reflectivity. The thickness of the Si/Ce and Ge/Si interface zones became asymmetrical owing to various effects occurring on the different atoms parallel to the direction of gravity-induced diffusion. The technique could prove useful for tuning physical properties of layered structures.

Strong-gravity experiments on Nd-Fe-B based magnet

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We investigate the effect of strong gravitational field on a Nd-Fe-B based magnet. The Nd-Fe-B based magnets show the highest maximum energy product among permanent magnets while the pure one shows the relatively low coercivity for applications. One of the solutions is to substitute heavy rare earth elements (HRE) such as Dy and Tb for Nd. However, HRE-free high coercivity Nd-Fe-B magnets have been required to be fabricated because of localized natural resource and high cost. Strong gravitational field can induce diffusion (sedimentation atoms) in multicomponent condensed matter. We performed a strong gravitational experiment (0.44×10^7 G at 400°C and 20 hours) on the Nd-Fe-B-based magnet. The X-ray diffraction pattern show that the peaks of the gravity experimental sample shifted. The gravity experimental sample was revealed that the coercivity a little increased. We are now under studying on investigating the gravity experimental sample.

Surface reactivity and mass transport in amorphous In-Ga-Zn-O

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Amorphous In-Ga-Zn-O gaining attentions because of its relatively high electron mobility compared to amorphous silicon and its affinity to flexible electronics. Although this compound has been developed as a useful channel layer of thin film transistors, charge compensation in this compound has not been well understood. A characteristic feature of this compound is high solubility of hydrogen. It has been reported that hydrogen concentration in this compound reaches on the order of percent. For controlling properties and designing fabrication processes, it is necessary to understand the defect chemistry and charge compensation phenomena in this compound. To this end, we performed isotope tracer study to reveal the surface reactivity and bulk mass transport behavior [1]. In particular, annealing the sample in humid atmosphere made with heavy water was employed. As a result we revealed that the surface reactivity of this compound is highly affected by post deposition annealing process and that oxygen diffusivity in this compounds was very fast even at relatively low temperature, e.g., 400°C.

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Study of the transport mechanism of Lithium ion in β alumina single crystal by NMR spectroscopy

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It has been known that Li β-alumina posses very high Li ion conductivity and therefore it can be a potential candidate as solid electrolyte in rechargeable battery. Therefore our study is devoted to the transport mechanism of Li ion in β-alumina single crystal. The frequency dependent conductivity was measured by AC impedance spectroscopy shows a small power law behavior ($\sigma \sim \omega^{0.106}$ to $\omega^{0.168}$) in the temperature range 303K to 203K [Chowdhury et.al J. Chem. Phys.140, 124509 (2014)]. We used pulsed field gradient (PFG) NMR to directly measure the macroscopic diffusion coefficient of Li ion in the β-alumina single crystal. The diffusion time (Δ) dependent diffusion coefficient was observed by PFG NMR which is corresponding to the frequency dependent of conductivity. A similar power law behavior was observed as $D \sim (1/\Delta)^{0.13}$, D is the diffusion coefficient of ^{7}Li. These results suggest that despite of being a single crystal, the structural inhomogeneity might present in β-alumina. From the dynamics point of view, this dispersion behavior reflects the presence of distribution of relaxation time in the β-alumina single crystal. The anisotropic nature of the translational diffusion of Li ion in the β-alumina crystal was confirmed from the angle dependent diffusion coefficient measurement by PFG NMR.

Oxygen nonstoichiometry, defect structure and oxygen diffusion in the double perovskite $GdBaCo_2O_{6-\delta}$

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Oxygen nonstoichiometry of $GdBaCo_2O_{6-\delta}$ was measured in the temperature range between 873 and 1273 K by means of thermogravimetry technique. The modeling of the defect structure was carried out and it was shown that the defect structure model proposed by us earlier and based on simple cubic perovskite $GdCoO_{3-\delta}$ is valid for $GdBaCo_2O_{6-\delta}$ up to temperature as low as 873 K.

Oxygen nonstoichiometry data allows precise calculating of the oxygen interphase exchange rate and tracer diffusion coefficient from the oxygen isotope exchange experiment. Oxygen diffusion coefficient calculated from dc-polarization technique with YSZ microelectrode is in very good agreement with oxygen tracer diffusion coefficient determined by means of oxygen isotope exchange with gas phase analysis method. Such agreement allows explaining significant scattering in the literature data on oxygen diffusivity in the double perovskite $GdBaCo_2O_{6-\delta}$ mostly by differences in the real composition or microstructure of the samples employed.

Steep increase of Li diffusivity in the anode material $Li_{4+x}Ti_5O_{12}$ at low amounts of Li insertion ($x = 0.1$, $x = 0.3$)

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Polycrystalline $Li_{4+x}Ti_5O_{12}$ (LTO, $0 < x \leq 3$) is one of the most promising, already commercially available, negative electrode materials for lithium-ion batteries showing a flat Li insertion plateau of about 1.5 V vs. Li/Li+; its theoretic specific capacity is approximately 175 mAh/g. The increased use of LTO is due to various properties such as low cost, satisfactory safety and easy preparation. Most importantly, upon Li insertion, the expansion of the material is almost negligible favoring a long cycle life. In samples with $x = 0$, Li self-diffusion, which can be microscopically probed via Li nuclear magnetic resonance, is rather low. With increasing Li insertion, however, the diffusivity increases significantly. This is accompanied by a redistribution of Li ions across the 8*a* and 16*c* sites in the spinel structure. Recent ^{7}Li NMR studies put emphasis on samples with Li contents of $x > 1$. As yet, there are, however, no information from NMR available answering the question of how Li self-diffusion changes when x is only slightly increased. The present results show that even at $x = 0.1$ ^{7}Li NMR spin-lattice relaxation, performed in the so-called rotating frame of reference, reveals a drastic enhancement of Li diffusivity, which is associated with a considerable reduction of the local hopping barrier pointing to the 8*a* – 16*c* – 8*a* migration pathway discussed in the literature.

Monte Carlo simulations for diffusion anisotropy in alkali feldspar

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Feldspar is one of the most common minerals of the earth's crust and is of high interest for earth sciences. Self-diffusion of potassium and sodium cations in alkali feldspar plays an important role in interpreting existing interdiffusion data and the observed great diffusion anisotropy. Despite the large number of studies, the basic diffusion mechanisms are not well understood. To study correlation effects on self-diffusion in the directions perpendicular to the (001) and to the (010) crystal planes a Monte Carlo method using the Mersenne twister pseudorandom number generator is highly suited. As a first approach, correlation factors f for alkali diffusion by a four-frequency vacancy mechanism in the alkali sublattice of the monoclinic feldspar structure have been calculated assuming that only one type of alkali cations is present. We find maximum f values of 0.5 and 0.25 for the directions perpendicular to the (001) and (010) planes, respectively. The findings will be compared to the results from radiotracer experiments using a ^{22}Na source and alkali feldspars of different potassium and sodium compositions.

Interdiffusion in the binary diffusion couples under a strong gravitational field

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Interdiffusion in the Cu-Brass (Cu:Zn = 7:3 at%) diffusion couples under a strong gravitational field was investigated. Under a strong gravitational field, the different body forces relative to the respective atomic weights of compounds can induce the sedimentation of atoms. In this study, we investigated the gravity-induced diffusion phenomena comparing with chemical potential diffusion. The Cu-Brass diffusion couple was prepared by electroplating method. Two samples whose interface was perpendicular (Upside: Cu Downside: Brass and Upside: Brass and Downside: Cu) to the gravity direction were centrifuged at 0.4×10^6 *G*, 400 °C for 60 hours. For comparison, the annealing experiment was performed at the same temperature and duration with the gravity experiment. The diffusion distance of two gravity samples whose upside: Cu and upside: Brass are 50 and 30 μm respectively while that of annealed sample was 35 μm. This may be caused by the sedimentation of atoms. We also perform the experiment of Kirkendall effect to discuss the diffusion mechanism. We are now under study.

MD Simulation of Ionic Crystal under Strong Gravitational Field

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While micro gravity field has been used in many fields, the materials science under a strong gravitational field, a million *G* level, is remained as unexplored field. Under strong gravitational field, one-dimensional body force is applied each atom in materials along the gravitational field, and displacements of each atom are induced. As the results, it is expected that unique molecular/crystal state is realized by the displacements. In this study, molecular dynamics simulation was performed to investigate unique crystalline states of ionic crystal under strong gravitational field. Interatomic interaction of Born-Mayer-Huggins type was adopted and potential parameters for anion and cation were empirically determined to reproduce lattice parameter and bulk moduli of the ionic crystal. Lattice vibration spectra along the gravitational field and the normal directions of the gravity were analyzed to confirm crystalline states of the ionic crystal. As the results, different shapes of spectra along the gravity are shown and the peaks of spectra along the gravity were shifted. It is shown that anisotropic lattice vibration spectra were induced by strong gravitational field, and it is insisted that the unique crystalline states and physical properties are induced by the gravity field.

Creation and evaluation of shocked Bi-superconducting structure under extreme conditions

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A shock compression is one of the methods of synthesis for polycrystalline oxide superconductors. Bi-Pb-Sr-Ca-Cu-O calcined powder is tightly encased into capsule, and shock pressure and heat are brought to the specimen by projectile launched by gunpowder. The crystal grains of Bi-based oxide superconductor grow by annealing process after shock compression. In order to obtain larger crystal grains and predominance of the Bi-2223 superconducting phases, shocked Bi-superconducting crystal grains, atomized with a jet mill, added into starting material as a seed crystal. The mixed powder is shock-compacted again, and the specimen becomes a superconducting bulk after the annealing process. In this research, specimens mixing rate of seed crystals was 5%, 10%, 15%, 20% and 25% were prepared. From SEM observation, the more seed crystals were contained, the larger crystal grains were found, in general. Furthermore, the huge crystal grains were found from the specimen mixing rate of seed crystal was 15%. From X-ray diffraction analysis, the more seed crystals were contained, the more peaks of Bi-2223 phase were observed. The shocked Bi-based oxide superconducting particles are expected as materials for thick films.

Formation of vanadium oxide (V-O system) graded compounds under strong gravitational field

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Strong gravitational field induces sedimentation or displacement of atoms by the different body forces acting on respective atoms, and gives a tool for controlling elemental compositions and structural change in condensed matter. Vanadium oxide (V-O system) has large contrast in phases like VO, V_2O_3, VO_2, V_2O_5 etc and shows the respective interesting diverse electrical, optical and magnetic properties. Strongly correlated vanadium oxides are currently considered as one of the basic functional materials having many applications in electronics, chemical and environmental technology. We performed a strong-gravity experiment on a V_2O_5 polycrystal using the high temperature ultracentrifuge at Kumamoto University. For the ultracentrifuged sample from strong gravitational field of 3.65×10^5 G at 400°C for 24 hours, it was found that VO_2 and V_2O_3 phases appeared by X-ray diffraction. VO_2 and V_2O_3 phases were increased while the V_2O_5 phase was decreased gradually along with the increasing strong gravitational field. The further investigations are now under study. The detail observation results will be shown in the conference.

Isotope distribution in AgI super-ionic conductor after centrifugation

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The ultracentrifuge experiments were performed on α-AgI super-ionic conductor samples. It was confirmed that all centrifuged specimens kept their stoichiometry. The isotope ratio of ^{107}Ag/^{109}Ag on specimens changed with negative gradient in the direction of centrifugal force. These results indicated that the heavy isotopes moved in the direction of the centrifugal force and the light isotopes moved in the counter direction keeping their charge balance in the specimen.

Bombardment induced ion transport – formation and analysis of electrodiffusion profiles

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The bombardment induced ion transport technique has been recently developed for investigating ion transport properties in solid electrolytes, polymers and polymer electrolytes. The method makes use of an alkali ion beam shining on the surface of the investigated sample. The impinging ions create a concentration and a potential gradient which induce the ion transport through the glass. An electrode at the backside of the sample is used to record the neutralization current.

If the sample is bombarded with an ion species that is not present in the glass prior to the bombardment (foreign ion bombardment) pronounced diffusion profiles can be created. These concentration profiles are subsequently analyzed by time-of-flight secondary ion mass spectrometry and modeled by means of the Nernst-Planck-Poisson theory.

Here, we have bombarded a series of calcium phosphate glasses containing a mobile alkali ion M1 = Na, K, Rb, Cs with low energy alkali ions M2 = Na, K, Rb, Cs with M1 ≠ M2. Thereby, the M1 ions are pushed towards the backside electrode and successively replaced by M2 ions. As one example we have shown that the diffusion coefficients for K+ and Rb+ in a mixed calcium phosphate glass depends on whether the glass was originally formed as a Rb+ glass or a K+ glass.

Lithiation/Delithiation of Ultra-Thin $LiCoO_2$ Films

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Thin films of $LiCoO_2$ were prepared by ion-beam sputtering and their capability to reversibly store and release lithium ions was proven by cyclic voltammetry and chronopotentiometry. In this talk, it is demonstrated that the lithium concentration of these films can be determined by a novel electrochromic absorption technique. This technique uses visible light and even allows measuring the time-dependence of the lithiation/delithiation reaction. Using this electrochromic absorption technique, the intercalation of lithium into the $LiCoO_2$ is studied in case of films between 10 and 400 nm in thickness. To quantitatively describe this intercalation process it is found that - apart from volume diffusion - the interface transport has to be taken into account, due to the very small thickness of the layers. Therefore, we suggest a diffusion model that considers the transfer of lithium ions from the liquid electrolyte into the $LiCoO_2$ layer. Using this model, we are able to accurately describe the experimental data. This allows determining the volume diffusion coefficient and the interface transport coefficient.

Increasing the Li Diffusivity of Poorly Conducting Solids by Mechanical Treatment

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Solid materials with a high ionic diffusivity are of vital interest in materials science due to their potential applications in secondary Li ion batteries. In many cases fast solid ion conductors are characterized by a large number fraction of defects that enable the ions to move over long distances. Reducing the crystallite size and introduction of structural disorder represent two very promising possibilities to tune the transport properties of otherwise poor ionic conductors.

Lithium aluminate, $LiAlO_2$, with an average crystallite size in the µm range, is known as a very poor Li ion conductor. Here, we show that its lithium ion conductivity can be increased by several orders of magnitude when the oxide is mechanically treated for many hours in a high-energy planetary ball mill. While the reduction of the crystallite size and the possible formation of amorphous $LiAlO_2$ was examined by HR-TEM and X-ray diffraction including SAXS and WAXS, the effect of high-energy ball milling on lithium ion dynamics in the aluminate was complementarily studied by both conductivity spectroscopy as well as Li NMR.

Using coherent X-rays to measure atomic-scale diffusion

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The increasing brilliance of synchrotrons in recent years allowed for extending dynamic light scattering to the X-ray regime, opening up the possibility to study dynamics of opaque materials down to the nanoscale. Due to the limitations of intensity even in the best synchrotron sources, X-ray Photon Correlation Spectroscopy is usually applied for small scattering angles. In our group we exhaust this technique by taking it to the wide-angle regime allowing us to study motion on the atomic scale. This talk will give an overview of how atomic-scale X-ray Photon Correlation Spectroscopy works and present recent results in glassy systems and in binary intermetallic alloys.

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Diffusion and solid state reaction in FePt thin films at low temperatures

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FePt thin films with additional third element (e.g. Ag, Cu, Au) are important materials for potential ultra-high density magnetic recording. In this contribution we present low temperature diffusion studies carried out in order to understand the diffusion intermixing and ordered phase formation mechanism in the Fe/Pt system also with Ag addition. Bilayer Fe/Pt and trilayer Fe/Ag/Pt films have been annealed below 400 °C. The structural properties of these samples were investigated by various methods including depth profiling with Secondary Neutral Mass Spectrometry, Transmission Electron Microscopy, and X-ray diffraction. It is shown, that first there is intermixing between Ag and Pt, while Pt segregates to the Fe/Ag interface. The intermixing of Pt and Fe takes place after the formation of the Ag-Pt mixed region. Finally homogeneous layers of FePt have been formed, although at the investigated temperatures the bulk diffusion processes are frozen. Additionally X-ray diffraction indicated that in both thin film systems the ordered $L1_0$ FePt phase, which is the requested phase for future magnetic data storage applications, is also present. Analysis of the depth profiles revealed evidence that the formation mechanism is based on a grain boundary diffusion-induced solid state reaction in which the reaction interfaces sweep perpendicular to the original grain boundary.

Nucleation in Cu/a-Si system

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Reactive diffusion in metal/Si thin films is interesting from a fundamental point of view. Solid state reactions start at the interfaces often after a quick low-temperature annealing. We used a combination of HRTEM and LA-APT [1] to characterize the nucleation/reaction in the a-Si/Cu system. We observed that the reaction between sputter deposited Cu and a-Si is strongly influenced by the deposition sequence [2]. If Cu is deposited on a-Si, an instantaneous reaction happens at low temperature, while silicide formation is delayed in the reverse case.

In this work we focus on the structure development at a-Si on Cu stacking. An increased roughness at the interface, the appearance of Cu rich particles in the a-Si bulk as well as spikes of high Cu contents protruding from the Cu layer is observed.

APT reveals that the composition of these precipitates (inside a-Si) differs from the Cu_3Si. HRTEM indicates the lattice spacing of the planes do not match the theoretical spacing for Cu_3Si phase. This indicates that, phase formation sequence might differ from literature suggestion.

[1] R. Schlesiger et al., Rev. Sci. Instrum., 81 (2010) 043703
[2] M. Ibrahim et al., Phys. Stat. Sol. C, 12 (2013) 1724.

Diffusion and interface controlled growth of nano-scale MgAl-spinel layers

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We investigated the growth of Mg-Al-spinel between MgO and Al_2O_3 in thin film settings with total thickness below 1 µm both on corundum and periclase substrates. Spinel growth was monitored in situ in a reaction chamber by synchrotron x-ray diffraction and ex-situ by FIB-TEM. We observe a transition from interface-reaction- to diffusion-controlled kinetics in the temperature range 900-1000°C on corundum substrates. On periclase substrate the same reaction is faster by about an order of magnitude, and starts at T at least 100°C below (800°C). Although we label the reaction $MgO + Al_2O_3 = MgAl_2SiO_4$ in our experiments "diffusion-controlled" other controls play a major role as well, as e.g. volume change and associated mineral strain.

Kirkendall effect in Copper-Nickel system on the nano scale

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Copper and its alloys are extensively used in numerous applications involving the area of the micro/nano-electronic devices. However, the diffusion processes in these materials still have many unanswered questions. Experiments were designed to investigate the Kirkendall effect on nano scale in CuNi thin films by means of secondary neutral mass spectrometry.

A set of Ni(30nm)/W(0.5nm)/Cu(70nm) and Cu(70nm)/W(0.5nm)/Ni(30nm) tri-layer were prepared by DC magnetron sputtering on SiO substrate. The 0.5 nm thick, non-continuous W film was used as Kirkendall marker. The annealing of the samples was performed at 525º C in vacuum. It has been found that the motion of Kirkendall marker does not occur in the annealed Ni/W/Cu system in spite of the considerable diffusional intermixing. On the other hand, the simultaneous appearance of two Kirkendall marker planes moving with different velocities was observed in Cu/W/Ni films. Detailed discussion of these experimental findings will be given.

Strain relaxation, vacancies and self-diffusion in thin nano-crystalline platinum films

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Nano-crystalline metal films for technical applications show after deposition a high amount of residual stress, which is an important characteristic of film/substrate combinations. We applied a dilatometry based approach using in-situ X-ray diffraction and reflectometry at the synchrotron to investigate the correlation between strain relaxation and modification of point defect concentration in thin nano-crystalline platinum films between 100 and 300 °C [1]. The results show that relaxation of compressive strain during isothermal annealing is correlated to a simultaneous creation of vacancies at the film free surface, proving the dominant role of vacancies for stress relaxation. Since, the self-diffusivity of Pt plays an important role for the kinetics of the process described above, we launched appropriate measurements. In order to cover a wide range of diffusion lengths we combined secondary ion mass spectrometry (SIMS) and neutron reflectometry (NR). While SIMS is sensitive to diffusion lengths larger than 10 nm, diffusion lengths down to 0.5 nm can be measured by NR. We used the stable isotope ^{194}Pt as a tracer and prepared ^{nat}Pt/^{194}Pt isotope heterostructures for the experiments. Preliminary results indicate an onset of volume diffusion at 600 °C, while for lower temperatures grain boundary diffusion dominates.

[1] W. Gruber et al., PRL 117 (2011) 265501.

Development of the new method of preparation of functionally graded thermoelectric materials by application of strong gravitational field

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In this study a novel method of preparation of functionally graded thermoelectric materials is presented. Application of strong gravitational field (up to 10^6 G) created in a special ultracentrifuge and elevated temperatures (up to 400-500°C) allowed sedimentation of chemical elements in $BiSbTe_3$ solid solutions in order to improve their thermoelectric properties.

Synthesis of raw materials was performed in a rocking furnace by melting of pure elements at the temperature of 700°C. Obtained ingots were milled into powders and formed by pulsed electric current sintering (PECS) into polycrystalline samples. Electrical properties of raw materials (i.e Seebeck coefficient and electrical conductivity) were investigated over the temperature range from 20 to 250°C. Thermal conductivity was measured using laser flash analysis (LFA).

For the analysis of influence of high gravity on phase and chemical composition changes XRD diffraction, and scanning electron microscopy SEM with EPMA analysis were applied.

The corresponding alterations of thermoelectric properties were investigated by a scanning thermoelectric microprobe STM. The results of our studies show that the new technique can be an effective method for preparation of the graded thermoelectric materials with a desired profile of carrier concentration.

Nucleation and Crystal Growth Experiments under Short-duration Microgravity using S-520 Rocket

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Sounding rockets have been developed and launched by ISAS/JAXA for more than 40 years. They have been dedicated to astrophysical observation, upper atmosphere exploration, space plasma physics, microgravity utilization, etc., for scientific research. The S-520 rocket has a flexible payload capability of 100 kg with 520 mm diameter and provides more than 5 minutes for a microgravity environment in its free-fall flight.

The S-520-24 sounding rocket was launched on August 2, 2008 for the following two crystal growth experiments; (1) FCT: morphological change in a faceted cellular array growth, and (2) DIA: diamond synthesis in hydrogen gas on a silicon substrate. The S-520-28 rocket was launched on December 17, 2012 for the following two nucleation experiments; (1) DUST: in situ visualization of nucleation environment in gas phase, and (2) CAL: detection of homogeneous nucleation of calcium carbonate.

In the crystal growth experiments, heat and mass transport process were visualized and it became possible to evaluate the kinetics on the growing crystal surface quantitatively. In the nucleation experiments, nucleation rate under microgravity was drastically decreased compared with that under the terrestrial condition.

$In_xGa_{1-x}Sb$ alloy semiconductor crystal growth under microgravity at International Space Station (ISS)

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Microgravity is a suitable condition to deeply understand the heat and solute transport phenomena, as the solute transport is diffusion dominant under microgravity. We have planned to study the growth kinetics by understanding the solute and heat transport of $In_xGa_{1-x}Sb$ alloy semiconductor, which is a promising material for thermo-photo-voltaic cells and infrared detectors, under microgravity and 1*G* condition. Recently one of the $In_xGa_{1-x}Sb$ crystals was grown on GaSb (111) A seed crystal using GaSb (111)A(seed)/InSb/GaSb (111)A(feed) sandwich sample under microgravity at International Space Station (ISS) and similar experiment was conducted with identical growth conditions under 1*G* condition. The results were comparatively analyzed. The dissolution lengths of seed and feed were smaller under microgravity compared to 1*G* sample, however, the grown length of $In_xGa_{1-x}Sb$ was larger under microgravity compared to 1*G* sample. Moreover, the interface shape of microgravity sample was almost flat, whereas the 1*G* sample had highly concave interface towards solution. The In composition of microgravity sample at seed interface was 0.029 and it was gradually decreased along growth direction. Whereas the In composition of 1*G* sample at seed interface was 0.041 possibly due to large amount of seed dissolution which shifted the interface position towards low temperature seed end. The experimental results were discussed by comparing the numerical results.

Heavy ion induced ERDA versus SIMS to study helium migration in pure iron

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Helium effects on microstructural and mechanical properties are key issues in fission or fusion materials research. Due to its extremely low solubility in most metallic alloys, helium strongly interacts with pre-existing and radiation-induced defects, leading to structures degradation. In order to extend the longevity of structural materials in the advanced reactors, it is necessary to comprehend the helium diffusion down to the atomic-scale.

Pure α-Fe samples were implanted with ^{4}He ions at 45 and 60 keV at room temperature at a fluence in the range 10^{16} - 10^{17} ions/cm^2. These implanted samples were then heated at different temperatures ranging from 400°C to 1000°C.

Helium depth profiles were then deduced either by heavy ion induced elastic recoil detection analysis (HI-ERDA) or by secondary ion mass spectrometry (SIMS). After implantation both techniques gave similar depth profiles in agreement with the projected ranges calculated by TRIM. The ^{4}He-depth profile evolution coupled with annealing treatments was also investigated. Advantages and drawbacks of these two experimental approaches are discussed taking into account the possibility to analyse He migration with sufficient accuracy to deduce kinetic properties and involved mechanisms.

High temperature diffusion in model Mn-Si/Fe thin film combinatorial libraries

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A Mn-Si-thin film combinatorial library was thermally co-deposited on Fe substrates for investigating the high temperature Fe-diffusion depending on the Mn-Si-composition. The subsequent annealing procedure was performed at different temperatures in the range of 600 to 900°C and various oxygen partial pressures down to about 5×10^{-24} Pa. The surface and the FIB-cross sections were analyzed before and after annealing by SEM, AES and XPS for identifying the diffusion and oxidation phenomena occurring on the surface as a function of the Mn-Si-composition. In order to study the thickness effects of individual elements on the overall diffusion process of Fe, thin film thickness gradients of Mn and Si were additionally evaporated using a slow moving shutter and annealed in the same conditions as the Mn-Si-library.

The results obtained from these model samples showed the differing oxidation behavior of the Si and Mn thin films and the diffusion of Fe depending on the library composition. The wide compositional range from about 15 at% - 75 at% Mn could partly be related to the diffusion phenomena occurring on the surface of steels alloyed with small amounts of Si and Mn (usually only up to 3%). Understanding those effects on idealized systems may lead to a better control of the steel production process.

Temperature dependence of ion-beam mixing in crystalline and amorphous germanium isotope multilayer structures

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The renewed interest in Germanium as base material for electronic applications has stimulated extensive experimental and theoretical studies. Successful integration of Ge in nanoelectronic devices requires fundamental understanding of ion-implantation-induced target modification and damage. In this contribution the temperature dependence of ion-beam mixing induced by 310 keV gallium ion implantation in crystalline and preamorphized germanium is reported. Isotopically enriched multilayer structures of alternating ^{70}Ge and ^{nat}Ge layers are used to visualize the self-atom mixing. The distribution of the implanted Ga atoms and the ion-beam induced self-atom mixing was determined by means of secondary ion mass spectrometry. Different temperature regimes of self-atom mixing are observed. Molecular dynamics simulations with a Stillinger-Weber type potential are used to study the self-atom mixing observed in the experiment. It is found that the dominant mechanisms of mixing are thermal spikes formed by transferring kinetic energy of the incident ion to the lattice. If the transferred energy is high enough, locally molten regions are created in which the atoms can move more freely compared to the lattice atoms. With increasing temperature the thermal spikes last longer and the mixing increases. This is in accord with the experimentally observed mixing behavior.

An Experimental Approach to Parameter-Dependent Lithium Ion Diffusion in a Viscous Liquid, poly(ethylene glycol)dimethyl ether (2500) by PGSE NMR Spectroscopy

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In the processes of our studies on the lithium ion diffusion measurements for sulfide-based solid conductors by pulsed-gradient spin-echo (PGSE) NMR spectroscopy, we experienced the lithium diffusion depends on the observation time and also the pulsed-field strength g. It is very curious and strange the g-dependent diffusion phenomena. Then, experimentally, we attempted to measure time- and g-dependent diffusion phenomena of lithium and solvent for a highly viscous liquid electrolyte by PGSE-NMR. The electrolyte composed of poly(ethylene glycol) dimethyl ester of molecular weight 2,548 and lithium bis(fluoeomethylsulfonyl)amine (Li-TFSA) became isotropic at high temperatures above 150°C, in which the time- and g-dependences almost disappeared. As the temperature decreased, the trend of the observation time dependent diffusion became more significant. Furthermore the diffusion phenomena were dependent on g in the region of the clear time-dependent conditions. For the long observation time under the high g-values in which enough the echo-attenuation was observed, the diffusion constant approached to an equilibrated value. The experimental g-dependent diffusion for a viscous liquid is quite anomalous, and theoretical approaches are waited.

Diffusion controlled crystallization of amorphous FeNiP in confined geometry

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Amorphous soft magnetic FeNiP is studied in confined dimensions regarding its phase stability and crystallization behavior upon annealing.

Therefore, porous Anodic Alumina Oxide (AAO) is used because it facilitates the control of regularity and shape of nanostructures via its pores which are uniform in length and uniform in diameter.

Upon in-situ annealing in the transmission electron microscope (TEM) the microstructural evolution could be analyzed. For comparison, ex-situ annealing was performed in a Differential Scanning Calorimeter (DSC) and in a vacuum oven.

Crystallization leads to a multilayer structure which crystal size depends on the confinement. Long range diffusion was observed following a phase separation of FeNiP in multilayers of FeNi and FeNiP phases after crystallization.

The impact of heating rates on the phase evolution is studied by controlled annealing with different heating rates of the FeNiP nanowires in N_2 atmosphere using a DSC.

The magnetic properties of the nanowire arrays have been characterized with a Vibrating Sample Magnetometer (VSM). The results will be discussed with respect to the different microstructures of the nanowire arrays caused by the different thermal treatments.

Investigating the "Grain Size Effect" on Grain Boundary Diffusion Kinetics in Nanocrystalline Copper: A Radiotracer Study

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Grain boundary diffusion kinetics of ^{63}Ni in nanocrystalline Cu samples with grain sizes, d, well below 100 nm (d ~35 nm and ~44 nm, respectively) produced by the Spark Plasma Sintering technique was investigated by the radiotracer method. The derived diffusivities, D_{eff}, are comparable to those determined in previous studies for Ni grain boundary diffusion in well-annealed, high purity, coarse grained, polycrystalline copper, substantiating the absence of a grain size effect on the kinetic properties of grain boundaries in nanocrystalline materials at grain sizes $d > 35$ nm. Furthermore, by application of a simple model (neglecting the effect of segregation), the analysis predicts that, if there exists an enhancement of triple line diffusion kinetics with respect to the corresponding grain boundary diffusion rate, it is less than $10^3 \cdot D_{gb}$ within a temperature interval from 420 K to 470 K.

Magnetoplastic Effect in Cu-Be alloys with additives of Ni

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Earlier authors [1] had been established a steady effect of appreciable microhardness increase of beryllium bronze BrB-2 after ageing in a constant magnetic field (CMF) which it is possible to refer as a magnetoplastic effect (MPE) in metal alloys. In the given work a brief overview of new data about the influence of Ni alloying additives on kinetics of artificial ageing processes of binary Cu-Be-alloys in CMF is given.

The analysis of the obtained experimental data shows that 1) imposing of CMF always leads to a "negative" MPE; 2) increase in Ni additive to alloy from 0.4 up to 1.0 wt. % leads to disproportionate increase of the microhardness of the Cu-Be alloy; 3) the reason of MPE occurrence and «magnetic memory» [2] in Cu-Be-alloy is atomic reorganization of atoms at phase formation stage at artificial ageing in CMF.

[1] J.V. Osinskaya, A.V. Pokoev. Fizika I Khimiya Obrabotki Materialov, No. 3 (2003), 18. In Russian.

[2] R. B. Morgunov, A. L. Buchachenko. Journal of Experimental and Theoretical Physicsl, 109 (2009) 434.

High-pressure torsion deformation of alloys in immiscible systems

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Although intensively investigated, the phenomenon of deformation-induced mixing of usually immiscible elements is still not well-understood. Materials obtained via severe plastic deformation methods, showing supersaturation or extended solubilities, sometimes related with amorphization processes, were described by several research groups. To investigate such materials and achieve a deeper understanding of deformation-induced interdiffusion mechanisms, powder consolidation and processing by high-pressure torsion was realized for Ni-Ag and Cu-Ag alloys. The generated materials stand out due to their uncommon microstructural constitution. Extremely small grain sizes down to a few nm are related with the occurrence of amorphization and characteristic so-called “non-equilibrium” grain boundaries. Modern TEM instruments, combining structural characterization with analytical methods, were used for detailed analysis. Besides conventional TEM techniques aberration-corrected high-resolution TEM imaging displayed grain boundary and defect structures. Scanning TEM mode gives chemical contrast in high-angle annular dark field images, identifying existing phases and homogeneity of the material. EDX line scans were placed across grain or phase boundaries in order to reveal the chemical configuration of the material on the nanoscale; thereby the degree of intermixing can be verified.

Helium behaviour in V-based materials analysed by means of TDS, TEM and SIMS

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Vanadium-based alloys are potential candidates for future nuclear systems due to their ballistic damage resistance. However, the helium accumulation at high temperatures in the structure induces embrittlement, thus limiting its application. One of the key factors is the extended self-point defects interaction with helium atoms, in particular thermodynamic and kinetic mechanisms involved in bubble nucleation and growth.

In order to understand the helium behaviour in pure V lattice, a multi-scale approach coupling different complementary techniques was employed i.e. Thermal Desorption Spectroscopy (TDS), Secondary Ion Mass Spectroscopy (SIMS) and Transmission Electron Microscopy (TEM). Pure V samples were irradiated by either 7 keV or 45 keV He+ ions at RT up to 1014 to 1016 He/cm2. TDS results showed different helium trapping mechanisms, indicating an effect of the dose and the implantation energy on He cluster thermal stability. Bubbles population was observed by TEM. In addition to these techniques, SIMS gave access 4He depth profiles as well as kinetic data after annealing treatments. These data were compared with pure Fe, well-known as the bcc model reference for nuclear materials.

This study contributes to a better knowledge regarding the complex helium effects during irradiation on the microstructural evolution in Vanadium-based alloys.

Deformation-induced mass-transfer in Cu-based alloys during high pressure torsion

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The influence of severe plastic deformation (SPD) on the formation and decomposition of solid solutions in several Cu-based alloys were studied. For this purpose the Cu–Co, Cu–Ag, Cu–In, Cu–Hf and Cu–Cr alloys with a concentration of a second component close to the maximal solubility at eutectic temperature Te were manufactured. These alloys were annealed (1) at high temperature close to Te where all (or almost all) atoms of a second component are solved in the Cu-rich matrix and (2) at relative low temperature where all (or almost all) atoms of a second component were precipitated in form of a particles of a second phase surrounded by an almost pure Cu-matrix. Such samples were subjected to the high pressure torsion (HPT) at 5 GPa, 5 rotation with speed of 1 rpm. The steady-state value of the torsion torque is reached in the studied Cu alloys already after 1.5-2 anvil rotations. The precipitates in samples (2) partially dissolved in the matrix during HPT. The solid solution in samples (1) partially decomposed. Both processes proceed extremely quickly. Various mechanisms of SPD-driven mass-transfer are discussed. The resulted concentration of a second component after HPT was almost the same in samples (1) and (2). In other words, the equifinal state is reached during HPT. The composition of Cu-matrix in this equifinal state is equal to that which can be reached in equilibrium after long annealing at a certain temperature T^{eff}. The T^{eff} (called effective temperature) is different in different Cu-based alloys. T^{eff} increases in the raw In → Ag → Co → Cr → Hf. In other words, T^{eff} increases with increasing activation energy of diffusion of a second component of its melting temperature.

Charging-induced defects in LiCo-oxide battery electrodes

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LiCo-oxide is a widely used cathode material of advanced battery systems. For minimizing performance losses and increasing cycle stability upon high degrees of Li extraction, an understanding of the processes of defect formation on the Li sublattice during battery charging is required. Positron annihilation has proven as a powerful tool to study vacancy-type defects even in such complex materials systems as battery electrodes. Recent studies of porous polycrystalline LiCo-oxide prepared by particle route reveal vacancy-type defects on the Li-sublattice the size of which increases with Li-extraction [1]. Moreover, indication for Li-reordering at the reversibility limit of extraction is found [1]. Initial measurements will be presented aiming at an extension of the studies on LiCo-oxide thin-films which are used as component of thin-film solid state batteries. Positron annihilation studies on these thin-film electrodes were accomplished by the high intensity slow-positron beam of the Heinz Mayer-Leibnitz neutron source in Garching. First results of depth-profile measurements of Doppler broadening of positron–electron annihilation radiation on LiCo-oxide thin-film samples of with various degrees of charging will be presented.

[1] P. Parz, B. Fuchsbichler, S. Koller, B. Bitschnau, F.A. Mautner, W. Puff, R. Würschum, Appl. Phys. Letters 102 (2013) 151901

Studying the phase growth in LiFePO4 thin films

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Lithium iron phosphate is a highly promising cathode material for modern lithium ion batteries, e.g. due to its outstanding cycling stability. According to current state of research, lithium is dissolved in the iron phosphate network and an attractive lithium-lithium interaction causes a phase separation into a lithium-poor and a lithium-rich phase. However, detailed studies about the influence of this phase separation on the electrochemical material properties are missing; e.g. the influence of phase formation and phase movement during a charge-discharge cycle. In this work, a kinetic mean field theory is used to simulate concentration profiles during the lithiation/delithiation of lithium iron phosphate thin films, applying various boundary conditions. Based on the concentration profiles, cyclic voltammetry curves are calculated for different scan rates and film thicknesses, respectively. These simulations are compared with experimental data that have been obtained at sputtered lithium iron phosphate thin films of excellent cycle life stability and well-defined film thickness. The comparison proves the validity of the kinetic mean field theory. Thus, the theoretical results allow a fundamental description about the kinetic behavior of lithium iron phosphate and a prediction of its electrochemical properties at different experimental conditions.

Molecular dynamics simulations of thermal transport in silicon isotope heterostructures

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The thermal conductivity of silicon (Si) can efficiently be reduced by isotope doping [1,2]. The advantage of this strategy is that it blocks the phonon transport while leaving the electric conductivity unaffected. The use of isotopically engineered silicon will increase the figure of merit of Si-based thermoelectric devices and might pave the way for future commercial products.

Non-equilibrium molecular dynamics simulations are performed to investigate the thermal transport in Si isotope heterostructures. The impact of layer thickness and interface roughness on the thermal conductivity of ^{28}Si/^{30}Si superlattices is studied. Additionally the thermal conductivity of a ^{28}Si/^{30}Si alloy is calculated. The temperature dependence of the thermal conductivities of the isotopically controlled structures is qualitatively compared to experimental results.

[1] H Bracht, N Wehmeier, S Eon, A Plech, D Issenmann et al., Appl. Phys. Lett. 101, 064103 (2012).
[2] H Bracht, S Eon, R Frieling, A Plech, D Issenmann, D Wolf, J Lundsgaard Hansen, A Nylandsted Larsen, J W Ager III and E E Haller, New J. Phys. 16 (2014) 015021.

Dislocation mass-transfer and electrical phenomena in metals at pulsing laser effect

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Influence of moving dislocations on mass-transfer and the phenomena, accompanying it in pulse-deformed metals is studied in a real-time.

Transport of self-interstitial atoms (SIA) by mobile edge dislocations in crystal with a cubic lattice is investigated by molecular dynamics. A strain rate (10^6 s^{-1}) and dislocation density (10^{10} – 10^{12} cm^{-2}) in a simulated crystal have corresponded to a laser effect in a Q-factor mode.

In FCC lattice under the stress influence SIA moves to an edge dislocation core, forming a system "dislocation+SIA". The fixed dislocations are the SIA sink, and moving dislocations accelerate the mass-transfer in a slide plane. A mass of propagating dislocations provides mass-transfer macroscopic depth. After SIA capture by a dislocation core the mass-transfer process is not thermal activated.

The experimental investigations in a real-time are performed by recording of electrical signal induced by the laser pulse irradiation of metal foils of different crystal structures.

The presence or absence of dislocations was provided by using the polycrystalline or amorphous metal foils, accordingly. There are distinctive features of the electrical signal waveforms obtained from the specimens with different structures. The signal amplitude recorded on the polycrystalline metal foil is larger than that for amorphous one. The peak amplitude was observed in the polycrystalline metal foil under laser giant pulse. This pulse generates the largest amount of moving dislocations in a polycrystalline foil. The obtained results confirm a dislocation-dynamic nature of generated electrical potential in pulse-deformed crystal.

Reactive diffusion behaviors in nanostructured metals produced by means of surface mechanical attrition treatment

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Reactive diffusion plays an important role in material industries related to metallurgy, electronics, and so on. A compound surface layer with modified mechanical and/or chemical properties might be formed on metallic materials by some methods in this way, such as nitriding, aluminizing, and galvannealing. Enhanced reactive diffusion kinetics is highly desirable to lower treatment temperatures and/or shorten the durations in these cases.

By means of surface mechanical attrition treatment (SMAT), grain sizes in the surface layer of various metallic materials have been refined into nanometer scale. In comparison with in the coarse-grained (CG) counterparts, significantly enhanced reactive diffusion kinetics has been observed in the nanostructured surface layers. For example, a much thicker layer of Fe-Zn compounds was formed in the nanostructured Fe electroplated with a Zn layer after annealing at temperatures around 300°C. The activation energy for the growth of the compounds layer decreased from ~167 kJ/mol in the CG sample to ~108 kJ/mol in the nanostructured sample. Furthermore, the Fe-Zn reaction in the nanostructured Fe showed a decreased onset temperature and an increased enthalpy change. The enhanced reactive diffusion kinetics will be discussed in terms of atomic diffusion and chemical reaction, which are expected to be promoted by various grain-boundaries and non-equilibrium vacancies in the nanostructured materials produced by SMAT.

Dopant diffusion and electrical activation in Ge during pulsed melting laser thermal annealing

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Germanium is the main candidate for replacing Si in future CMOS devices due to the higher mobility of charge carriers. In order to fulfill the future technological nodes, ultra-shallow junctions with electrically active levels overcoming the solid solubility of dopants are required. Pulsed laser thermal annealing (LTA) in the melting regime is a promising approach, because of its potential capability of increasing the dopant activation and reducing the diffusion paths.

Ge samples implanted with B or As and followed by LTA (with different energy densities and multiple pulses) were characterized by SIMS, SRP, TEM and HRXRD [Impellizzeri et al. J. Appl. Phys. 113, 113505 (2013); Milazzo et al. J. Appl. Phys. 115, 053501 (2014)]. The observed anomalous dopant redistributions were simulated on the basis of a two diffusivity states of Ge in the liquid phase [Fisicaro et al. Phys. Rev. Lett. 110, 117801 (2013)] as well as of non-equilibrium segregation at the liquid/solid interface. Although for As a new record of activation (1.1×10^{20} cm^{-2}) has been established, dopant clustering and interaction with oxygen contamination diffusing from the native Ge oxide are shown to be crucial issues for improving LTA implementation in advanced Ge-based devices.

Diffusion Behavior of Nitride ion in GaN Thin Films

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We are studying on relationship between defect structure and electric properties in GaN thin films with the wurtzite crystal structure. GaN thin films was grown by a MBE method. Using isotopes, i.e. ^{15}N for GaN, isotopic hetero-structure were synthesized. The diffusivity of anions in wurtzite structure was evaluated by means of a secondary ion mass-spectrometer. According to the results, the diffusion coefficient was affected by strains in thin films. We will discuss about the defect structure and some electric properties.

Dislocation relaxation processes in high-purity molybdenum and less-purity molybdenum

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Dislocation relaxation processes due to motion of non-screw dislocations and screw dislocations are observed in pure body centered cubic metals. Typically, alpha and gamma peaks have been observed in internal friction measurements of high-purity molybdenum (S. Suzuki and A. Seeger: Phys. Status Sol.(a), 131(1990), 727), and these peaks were assigned to motion of non-screw dislocations and screw dislocations. However, when there are impurities such as a small amount of carbon in molybdenum, they suppress appearance of the relaxation peaks by pure dislocations. Instead of such dislocation relaxation peaks, it has been shown that a broad relaxation peaks appears in molybdenum containing residual carbon. Since the dislocation is thermally instable at measurement temperatures, the kinetics of the relaxation strength was investigated by isothermally annealing. The activation enthalpy for the relaxation indicates that the broad relaxation peak may arise from diffusion of carbon to dislocations. Another relaxation peak was also found in samples after annealing at high temperatures. The relaxation process also exhibits to be related to diffusion of carbon in molybdenum. In the presentation, these relaxation characteristics due to the dislocation motion and the interaction between carbon and dislocations in molybdenum are discussed.

Influence of the annealing atmosphere on the structural properties of FePt thin films

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Chemically ordered $L1_0$ FePt is a potential material candidate for ultra-high density magnetic data storage due to its large magnetic anisotropy, high saturation magnetization, and high corrosion resistance. In this study, we have investigated the influence of the annealing atmosphere using N2, Ar, and forming gas ($Ar+H_2$ (3 vol.%)) for annealing temperatures up to 900°C on the structural properties of FePt thin films by x-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

Irrespective of the annealing atmosphere, the chemically ordered $L1_0$ FePt phase has formed after annealing at 500°C. Higher annealing temperatures in N_2 or Ar atmosphere resulted in a strong increase in grain size and surface roughness but also in the appearance of a pronounced (001) texture in the FePt films [1]. However, these films show the presence of iron oxide. In contrast, annealing in forming gas atmosphere suppressed the oxidation process and resulted in a reduced grain size and lower surface roughness. However, no (001)- but a strong (111)-texture was obtained after annealing at 700°C, which might be related to the reduced unit cell tetragonality and incorporation of hydrogen to the FePt lattice. Thus, this study clearly demonstrates that the oxygen/hydrogen content plays an important role in controlling the crystallographic orientation during post-annealing.

[1] I. A. Vladymyrskyi et al., J. Appl. Phys. 114, 164314 (2013).

Depletion Process of Manganese in Surface Layers of Shape Memory Fe-Mn-Si alloys by Annealing

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Austenitic Fe-Mn-Si alloys containing a large amount of manganese exhibit the shape memory effect. In these alloys, the fcc austenitic phase is transformed to the hcp martensitic phase by deformation at room temperature, and its reverse transformation occurs by heating. This phase transformation is martensitic transformation, in which shear microscopic deformation is observed. As the stability of these shape memory alloys is dependent of the amount of manganese, it is to be noted that the composition of manganese in the alloys is not changed during processing. Typically, manganese can be evaporated from the surface of these high manganese alloys during annealing, since the vapor pressure of manganese is high. Actually, it has been shown that manganese is depleted in surface layers of the alloys during annealing at high temperatures. In this study, the depletion of manganese induces the phase transformation of the fcc austenitic phase to the bcc ferritic phase in surface layers of this alloy. From analysis of the surface layers of the ferritic phase, it was considered that the depletion process of manganese is fundamentally controlled by diffusion of manganese in the alloy.

Electric phenomena in metals under the conditions of impulse mechanical loading

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Atomistic mechanism of anomalous mass-transfer in metals and alloys under the conditions of impulse loading represents a long-standing issue. The mass-transfer coefficient (in an analogy to the common diffusion coefficient) is equal to or even exceeds the atomic mobility in the liquid and gaseous phases in dependence on the loading parameters. Further insights into underlying mass-transfer and deformation processes can be provided by a real-time detection of the differences of electrical potentials of metals during the impulse loading. The present work is aimed to correlate the electromagnetic phenomena and anomalous mass-transfer in metals and alloys.

The investigation is performed on pure metals (Fe, Ni, Cu) and alloys (steels 3 and 12X18H10T). The deformation velocity ($\dot{\varepsilon}$) is varied in the range from 10 to 10^3 s^{-1}. The mass-transfer parameters are determined by the isotope-tracers method (^{63}Ni and ^{59}Fe), the processing temperature, T, is kept constant at 77 K or 293 K.

It is shown that a difference of electric potentials appears under shock loading accompanied by plastic deformation, and its magnitude for different metals approaches the values of 0.5 to 10 mV. The effect is maximal for the steel 3 and minimal for Cu. The mass-transfer coefficients, Dm, adopt the values from $0.6 \cdot 10^{-8}$ cm^2/s to $1.3 \cdot 10^{-8}$ cm^2/s (particularly for Fe in the steel 3, $T = 293$ K, $\tau_{imp} = 10^{-2}$ s).

The amplitude of the electric signal versus the imposed deformation, ε, reveals a few maxima for pure Fe and the steel 3. An increase of the deformation rate leads to both, an increase of the penetration depths of diffusing atoms and a growth of the amplitude of electric signals, and corresponding dependencies follow quadratic laws. A correlation of the size of the mass-transfer-affected zone and the magnitude of electric impulses is found. An increase of the loading temperature from 77 to 293 K affects the signal amplitude, namely it is decreased in Fe and the steel 12X18H10T, it is slightly increased in Ni, and it grows by a factor of three in the steel 3.

The amplitude of the electric current is a quadratic function of the deformation rate under impulse loading and it approaches a value of 10^{-3} A/m^2.

The physical models considered here fit to a certain extent well into the “ambipolar diffusion” concept. Whereas this concept is applicable to diffusion in plasma, we suppose that it can be used in the case of impulse mechanical loading in metals, too. A metallic system can be represented as ion cores immersed in an electric fluid (plasma’s analogue). The electrons and the ions start to move under impulse load under an action of stresses. Light electrons move substantially faster than heavier ions. As a result, a redistribution of charges appears and an electric potential is created. The subsequent decay of the induced potential is driven by the system equilibration.

Competition of Kirkendall shift and Kirkendall voiding during inter- and reactive diffusion

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Void formation at the contact of two components leads to contact instability and affects the mechanical properties of materials and compounds.

Computer model for the voids growth in the diffusion zone of a binary diffusion couple and in the bulk of the single component taking into account the competition between Kirkendall (K) sinks (dislocations) and Frenkel (F) sinks (voids) of vacancies irrespective of the reasons for vacancy supersaturation is proposed.

The dependence of the average radius of the voids on the mean free path of the vacancies is found. Evolution of the void size distribution at different mean free paths of the vacancies during the process of inter- and reactive diffusion has been modeled.

With the increase of the mean free path of the vacancies (K-sinks):

- the voids (F-sinks) reach larger average radii during interdiffusion process. The increase of the maximum radius of the voids depending upon the mean free path of the vacancies, as well as the change of the width of the void growth zone, proceeds according to the power law.

- the voids reach less average radii during reactive diffusion process. The cubic average radius grows linearly with time.

SIMS as a new methodology for analyzing helium depth profiles in bcc metals

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Helium effects on microstructural and mechanical properties are key issues in fission or fusion materials research. Due to its extremely low solubility in most metallic alloys, helium strongly interacts with pre-existing and radiation-induced defects, leading to void swelling, hardening, creep rupture, blistering and surface exfoliation. In order to extend the longevity of structural materials in the advanced reactors, it is necessary to comprehend the helium diffusion down to the atomic-scale.

Recently, secondary ion mass spectrometry (SIMS) allowed the determination of the helium distribution after implantation and annealing treatments in iron samples. The Cs+ primary ion beam coupled with CsHe+ molecular ions detector is a promising technique which overcomes the very high He ionization potential. Furthermore, this approach provides a higher resolution compared to depth profiling methods, such as ion beam techniques.

In this study, SIMS experiments were performed by similar techniques in implanted monocrystalline and polycrystalline vanadium samples. The implantation ranges of 45 keV He ions were in agreement with the projected ranges calculated by TRIM. The 4He-depth profile evolution coupled with annealing treatments was also investigated. This study confirmed the great potential of this experimental procedure as a direct He-depth profiling technique in bcc metals.

Centrifugal Effect on Diamond Synthesis by CDV Process

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Generally, diamond produced by chemical vapour deposition (CVD) is synthesized using a flow system. However, carbon source was almost evacuated before reaction of diamond synthesis. On the other hand, diamond synthesis in a closed system instead was first reported in 1997. Growth rates achieved using a closed system was superior to those achieved with a flow system. It is well known that buoyancy-driven convection has an influence on diamond synthesis with CVD. However, buoyancy-driven convection in a closed system has not yet been investigated in depth under controlled conditions. Buoyancy-driven convection is controlled by high gravity with rotating centrifuge.

In this presentation, the authors will report diamond synthesis by CVD in a closed system on a centrifuge to evaluate centrifugal effect of enhanced/suppressed buoyancy-driven convection during diamond deposition. The deposition length of synthesized diamond was observed by a high temperature CCD camera. The deposition length was increased in over 3.0*G* of acceleration, where 1.0*G* = 9.8 m/s^2, on the other hand, decreased in from 1.4*G* to 2.0*G*, in which buoyance-driven convection was damped by the centrifugal effect.

Finite element analysis of the grain size effect on diffusion

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Thermochemical treatments like carburizing or nitriding are nowadays widely used in industrial processes. Their main interest is to increase wear and fatigue resistance on the surface of metallic parts, and to restrict any geometrical variations or to avoid any phase transformation of the material. However, the efficiency of such techniques is still constrained by the diffusion mechanisms of chemical species: to reach a sufficient depth in a relatively short time, it is necessary to perform thermochemical treatments at high temperature.

The WINOA Company has developed a severe plastic deformation process derived from shot peening which leads to a strong grain size refinement on the top surface to a nanometric scale. One of the effects of such technique is to significantly improve the thermochemical treatments efficiency. It especially improves the diffusion kinetics and can modify the state of precipitation in the material.

In the automotive and aeronautic industry, implementing a new process requires to have a minimum level of prediction tools. That's why this work aims at understanding the grain size effect on diffusion kinetics with Finite Element simulations. Homogenization techniques are used on representative cells with different grain size to build a formal relationship between macroscopic diffusivity and grain size.

Magnetodiffusional Effect in Ferromagnets in the Constant and Pulsed Magnetic Field

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Review of experimental data on the heterodiffusion in ferromagnetic materials – Fe and Co – in various structural and magnetic states under imposing of a constant and pulsed magnetic field (MF) is presented. These data show, that constant and pulsed MF noticeably influences the macroscopically measured diffusion coefficient. The interrelation between the observed diffusive phenomena and the magnetoplastic effect [1] which is influenced by available spin properties and interactions of defects in MF is discussed.

The range of possible types of defects in the case of ferromagnets is wider: the defects of magnetic structure and phenomena of magnetostriction, magnetic anisotropy of the diffusion matrix and magnetic relaxation [2] should be additionally taken into consideration.

Possible mechanisms of influence of constant and pulse MF on the measured characteristics in view of interaction of moving domain borders, dislocations and impurity atoms are discussed.

[1] R.B. Morgunov and A.L. Buchachenko: Physical Review B 8, 014115 (2010).
[2] A.V. Pokoev, A.A. Fedotov, in: Diffusion, Stress, Segregation and Reactions, (International Workshop, Svitanok, Ukraine, June 1-7 (2012)), p. 2012.

Reactive diffusion in UO_2-Gd_2O_3-system

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Human civilization can not exist without energy. The struggle for power sources becomes dominant in the survey of natural resource management. At the present stage of human development, nuclear energy is the undisputed leader among energy sources for mankind.

Now, most of the energy is generated by thermal reactors, operated in nuclear power plants, fueled which is UO_2. To improve the economics of nuclear thermal reactors used fuel with burnable neutron absorber. Typically, fuel is UO_2 doped Gd_2O_3.

We have studied the reactive diffusion in the system UO_2 - Gd_2O_3. Samples were obtained by SPS-sintered uranium dioxide and gadolinium oxide powders. Diffusion annealing conducted at temperatures of 1500 – 2000°C. The region of maximum solubility and chemical composition of the compound formed in system are investigated. The diffusion coefficients and the activation energy of the process are determined.

Investigation of intermediate phase layers growth in the interdiffusion of metal system Cu-Cd

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A number of investigations have shown that in certain cases the phases apparent in equilibrium phase diagrams will not emerge in the diffusion zones of real samples. This occurs most frequently in zones with narrow field of homogeneity. As the mechanism behind such phenomena is not yet fully understood, further experimental and theoretical investigations are necessary.

The interdiffusion process in multiphases of binary metal system Cu-Cd has been studied. The experiments have been carried out at temperatures below the eutectic (300 °C), with variation of the annealing time from 2 to 192 h. The structure of the diffusion zone and distribution of concentration have been studied by metallographical analysis, optical microscopy, scanning electron microscopy and electron probe microanalysis. The experimental results of the growth rate and diffusional permeability of phases with a narrow field of homogeneity have been compared to earlier results.

Kirkendall effect in the multiphase ternary Ni-Cr-Al system

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The Kirkendall effect due to interdiffusion in the ternary Ni-Cr-Al system is investigated. In the experiment, the diffusion multiples were prepared by hot isostactic pressing (HIP at 200 MPa and 1473 K. Thanks to this, good, oxide-free junctions were obtained. HIP method allowed place ThO2 markers of contact interfaces and obtain good junction between terminal alloy compositions.

The Kirkendall effect was examined by measuring the distance change between two marked planes. The experimental results were used to validate the predictions of theoretical calculations performed within the bi-velocity phase-field method.

Effect of recrystallization on diffusion in ultrafine grain Ni prepared by high pressure torsion

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The effect of recrystallization and grain growth on grain boundary self-diffusion is studied in ultrafine-grained (UFG) Ni prepared by high-pressure torsion. Two Ni materials of low (99.6 wt.%) and high (99.99 wt.%) purity levels are investigated. The ultrafine grain structure of less pure Ni remained stable during diffusion annealing, whereas recrystallization and subsequent grain growth occurred in high purity Ni at the same annealing conditions. The kinetic properties of stationary and mobile grain boundaries are examined in detail. It is shown that while similar ultrafast diffusion rates are measured in the samples of both purity levels (even after recrystallization is completed), unusual concentration profiles with characteristic "kinks" are observed for Ni self-diffusion in 99.99 wt.% pure Ni, which undergoes recrystallization during diffusion annealing treatment. This behavior is found to be related to specific kinetic properties of grain boundaries which encompass the recrystallized areas and consume numerous defects of the UFG matrix during their fast motion. A model of self-diffusion in recrystallizing material which takes into account a hierarchy of stationary and moving fast diffusion paths is proposed and its satisfactory agreement with the experiment is demonstrated. The nature of ultrafast diffusion paths in UFG Ni and the reasons of their unusual stability against recrystallization annealing are elucidated.

Nanoscale investigations of solid state reactions and shift of individual interfaces in Ni/amorphous Si system by Secondary Neutral Mass Spectrometry

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Heat treatments of nanocrystalline Ni(20 nm)/a-Si(50 nm), Ni(5%Pt)(20 nm)/a-Si(50 nm) as well as Ni(5%Pt)(40 nm)/a-Si(100 nm) systems at 180°C and 200°C were carried out in vacuum (10^{-6} mbar) for different annealing times. Depth profiles obtained by Secondary Neutral Mass Spectrometry allowed determination of the positions of the individual interfaces of Ni_xSi_{1-x} product layer. The kinetics of the shrinkage of the initial nanocrystalline Ni film and the amorphous Si film as well as the average growth kinetics of the product phase were determined in the very early stage of the solid state reaction. These kinetics followed the parabolic growth law i.e. the change of the thicknesses were proportional to $t^{1/2}$. Effect of Pt on the enhancement of the homogeneity and the growth kinetics is also presented.

Effect of megagravity-induced anion height change in iron-based superconductors

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We report on the effect of megagravity-induced anion height change in iron-based superconductors. In iron-based superconductors, it has been pointed out that the superconducting transition temperature depends on the anion height between Fe and anions. We investigate properties of iron-based superconductors with the anion height changed by megagravity and discuss the anion height dependence of the superconducting transition temperature.

Bombardment Induced Ion Transport: structure and composition dependence of the DC-conductivity in Calcium-phosphate glasses

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The ion transport of potassium and rubidium ions through alkali-calcium-phosphate glasses (X% CaO - (55-X) M_2O - 45% P_2O_5 [X = 20, 30, 40; M = Na, K, Rb]), i.e. glasses differing in the kind and the content of mobile carriers, has been studied using the bombardment induced ion transport (BIIT) technique. The results are compared to impedance spectroscopy (IS). The BIIT method makes use of an alkali ion beam shining on the surface of the investigated sample. The impinging ions create a concentration and a potential gradient which induce the ion transport through the glass. An electrode at the backside of the sample is used to record the neutralization current.

If the sample is bombarded with an ion species present in the glass prior to the bombardment (native ion bombardment) specific conductivities can be accessed.

In the present study, the specific conductivity, the activation energy, the mass and ion density and the glass transition temperatures are discussed as a function of the composition and structure of the glass.

Crystallization and reconstructive layer transformation of a-Si/Au multilayer thin films under a strong gravitational field

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The needs to fabricate the high quality poly crystalline Si thin film is growing, with increasing performance of large area electronic devices such as thin film solar cells, liquid crystal display, etc. In the recent days, the new method was developed that is to fabricate the high quality poly crystalline Si thin film from amorphous Si/Au bilayer thin film with lower annealing temperature than conventional Si recrystallization temperature. In that recrystallization process, Si layer and Au layer exchange their positions. However, the mechanism of this phenomenon is thought to be explained by the MIC (Metal Induced Crystallization) of Au and very low solidification limit of Au into crystal Si. There are some unclear questions.

In this paper, we would like to discuss the effects of strong gravity on recrystallization. Using high-temperature ultracentrifuge system, it is possible to anneal samples up to around 800 K under up to around 560,000 G. It was reported that concentration of solid was varied by difference of specific gravity of constituent atoms under the such strong gravitational field. We have made some samples (bi-layerd Si/Au thim films, multi-layered Si/Au thim films) and found the effects of strong gravity.

Interface Kinetics in Thin-Film Lithium Ion Batteries

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Thin film lithium batteries (TFBs) are regarded as next generation's energy storage devices. They are capable of being utilized in highly specialized applications such as implants, wireless nodes, or circuit boards.

Based on this, we investigate a novel kind of TFB that makes use of high-performance materials. In particular, we are using thin films of $LiFePO_4$ as cathode electrode, LiPON as solid electrolyte, and silicon as anode electrode. All of these materials are prepared by sputtering in order to achieve high quality and uniform layers.

Since battery capacity strongly depends on the properties of electrodes, all battery components were synthesized and studied, separately. They were characterized by means of transmission electron microscopy, cyclic voltammetry, chronopotentiometry and impedance spectroscopy. Afterwards, corresponding multilayer stacks were studied. In these studies it turns out that the deposition of the solid electrolyte is most critical. Since lithium ions have to pass through the interfaces between the solid electrolyte and electrodes, these interfaces quality is crucial to determine battery life time and maximum current density.

Phase evolutions in AuCu/Sn system by solid state reactive diffusion

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The interfacial reactions between several Au(Cu) alloys and pure Sn were experimentally studied at 200°C. The amount of Cu in $AuSn_4$ and $AuSn_2$ phases was found to be as low as 1 at.%. Based on the experimental results there is no continuous solid solution between (Au,Cu)Sn and $(Cu,Au)_6Sn_5$. Copper content in the (Au,Cu)Sn was determined to be about 7-8 at.%. A significant amount of Au in the $(Cu,Au)_6Sn_5$ and $(Cu,Au)_3Sn$ phases was observed as well. Besides, two ternary compounds were formed, (i) one with a stoichiometry varying from $(Au_{40.5}Cu_{39})Sn_{20.5}$ to $(Au_{20.2}Cu_{59.3})Sn_{20.5}$ (ternary 'B') and (ii) other with a composition of $Au_{34}Cu_{33}Sn_{33}$ (ternary 'C'). The measured phase boundary compositions of the product phases are plotted on the available Au-Cu-Sn isotherm and phase equilibria are discussed. It is found that the complexity and the average thickness of the diffusion zone decrease with an increase in Cu content except for the Au(40at.%Cu) couple.

Interface Reactions in LiPON-Based Thin-Film Batteries

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Complete thin-film solid state lithium ion batteries were prepared by deposition of thin LiPON layers between two metal electrodes. After applying some external voltage to the electrodes, electrochemically active interface regions develop, serving as anode and cathode, respectively. Therefore, the samples operate as full-functional thin-film lithium ion cells. The properties of these cells were investigated using transmission electron microscopy, cyclic voltammetry, and electrochemical impedance spectroscopy. In particular, the characterization of reactive layers between an Ag electrode and the LiPON layer was subject of research. To this aim, thin LiPON layers were obtained by reactive magnetron sputtering of Li_3PO_4 in nitrogen atmosphere, in addition to a Pt and an Ag electrode. These thin-film cells feature a thickness of only about 700 nm. First results on the microstructure of the cells show that nanocrystalline Ag precipitations develop at the interface between LiPON and Ag. The volume of this interface reaction region increases with increasing number of charge-discharge cycles of the electrochemical cell.

Ga penetration in ultra-fine grained Al synthesized by severe plastic deformation

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Fast penetration of a liquid into the grain boundary network of a polycrystalline solid is leading to embrittlement, which is observed for different metallic or ceramic couples. A well-known example is the catastrophic embrittlement of Al upon penetration of initially liquid Ga along Al grain boundaries. This effect occurs even at room temperature; below the melting point of Ga. Severe plastic deformation (SPD) of Al is known to refine the grain structure, introducing a high density of grain boundaries of different type. In this study the penetration of Ga along grain boundaries of fine grained Al produced by the SPD method of high pressure torsion is analyzed. Upon applying a droplet of liquid Ga to the SPD Al surface, the penetration process was studied using dilatometry, atomic force microscopy (AFM) and scanning electron microscopy (SEM) including electron-backscatter diffraction (EBSD). A two-stage process was observed in the dilatometer. The developments of the grain boundary decoration by Ga and the surface evolution have been examined by SEM and AFM. The microstructure changes induced by the Ga penetration are characterized by EBSD, to monitor the evolution of the grain size, orientation and the grain boundary misorientations. The results are discussed with respect to previous works to gain information on the underlying mechanisms that control the Ga penetration.

Grain boundary diffusion induced reaction layer formation in Au/Cu thin-film system at the low temperatures

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Using secondary neutral mass spectrometry, X-ray diffractometry and transmission electron microscopy grain boundary diffusion induced reaction layer formation, GBDIREAC, was investigated in the Au/Cu thin film system at low temperatures, where the bulk diffusion is frozen. The process starts by grain boundary interdiffusion and after the filling up grain boundaries the reaction starts here leading to the motion of the newly formed interfaces perpendicular to the grain boundary plane. Finally, the complete homogenization, leading to formation of intermetallic phases, finishes when all the pure components have been consumed. In Au(25nm)/Cu(50nm) samples the final state is the ordered $AuCu_3$ phase. Decreasing the film thicknesses to Au(10nm)/Cu(25nm) results in the acceleration of the diffusion process. Changing the thickness ratio either a mixture of Cu-reach AuCu disordered and $AuCu_3$ ordered phases, or a mixture of disordered Cu- as well as Au- reach solid solutions can be produced. Using a simple model the interface velocity in both the Cu and Au layers were estimated from the linear increase of the average composition and its value is about two orders of magnitude larger in Au (10^{-11} m/s) than in Cu (10^{-13} m/s).

Diffusion Controlled Grain Boundary and Triple Junction Wetting in Polycrystalline Solid Metal

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In this work were investigated the processes of formation and spreading in solid metal along grain boundaries and triple junctions the channels net of another but liquid metal. As solid components of the system were used the samples of the polycrystalline copper with the grain size about 100 nanometers. The copper samples were wetted by bismuth melt. It was obtained the time dependences of the liquid net depth at several temperatures. The experimental data indicate that the limitative stage of the liquid net growth process is the diffusion stage – grain boundary diffusion or triple junction diffusion.

General approach to diffusion under a stress in metals and interstitial alloys

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One of the chief aims of our work is to obtain general equations for the diffusion fluxes under strain that give the possibility for using these equations at low temperatures, as in this case the strain influence on the diffusion fluxes is manifested in maximal degree. Our approach takes into consideration, that the strains can alter the surrounding atom configuration near the jumping one and consequently the local magnitude of the activation barrier and a rate of atom jump. The rates of atom jumps in different directions define the flux density of the defects. Now we take into account, that strain values are different in the saddle point and in the rest atom position, in differ from our consideration that was done by us earlier. As a result in the development of our approach the general equations for the vacancy fluxes and impurity fluxes are obtained for fcc and bcc metals. These equations differ sufficient from ones that was obtained earlier. In our presentation we are going to discuss the main features of the theory of diffusion under stress and its applications.

Interdiffusion: consistency of Darken's and Onsager's methods

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For the first time the consistency between Darken method and Onsager theory is presented. Nernst-Planck flux formula is used in Darken's method to obtain the interdiffusion fluxes. The effective interdiffusion potentials, derived for the independent components in the system, allow obtaining the symmetrical matrix of the interdiffusion coefficients. The transport coefficients for 2, 3 and *r*-component system are provided. The obtained results are interpreted in the light of Onsager's theory of irreversible thermodynamics and the entropy production due to the interdiffusion process is given. The presented approach allows to derive Onsager's phenomenological coefficients for the interdiffusion in an explicit form, which is directly correlated with the mobilities of the atoms present in the system.

Na-K interdiffusion in alkali feldspar: composition dependence, anisotropy, and the influence of lattice strain

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Cation exchange experiments were conducted using oriented plates of sanidine as starting material. The formation of interdiffusion fronts propagating into the sanidine by Na-K-interdiffusion on the alkali sublattice was observed. The diffusion fronts are highly anisotropic with fronts normal to (010) being significantly sharper than fronts normal to (001). The observed geometry of the diffusion fronts can be explained by a composition dependence of the interdiffusion coefficient D. The composition dependent D was determined in the composition interval XOr 0.65 to 1 and for the directions normal to (001) and (010) from the composition-distance using the Boltzmann transformation.

We found interdiffusion to be roughly constant in the composition interval XOr 0.65 to 0.95 and then rise steeply for both directions. Normal to (001) interdiffusion is faster by a factor of about ten than normal to (010).

Comparison with theoretical calculations of D from self-diffusion data from literature using the Nernst-Planck relation shows a rough fit for interdiffusion normal to (001), while interdiffusion normal to (010) deviates significantly from what would be expected.

Due to the composition dependence of the lattice parameters of alkali feldspar, any shift in composition leads to elastic strain. The cross-correlation-technique was employed to determine the strain distribution across the observed interdiffusion fronts.

Ni grain boundary diffusion in Cu-Co alloys

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The Co effect as an alloying element on grain boundary diffusion (GBD) in Cu attracts particular interest due to anomalous GBD of Co in Cu. This talk discusses the influence of Co (up to 2.5 mass.%) on NI GBD in Cu at temperature range 500 – 700°C. Neither all values of the triple product GBD, obtained by XPS-method, nor the activation energies are not essentially different from literature data for Ni GBD in Cu. Because GBD is a structure-sensitive property, from this result it follows that Co does not change the GB structure.

Self diffusion in Al_2O_3

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Self-diffusion in aluminum oxide (alumina, α-Al_2O_3) has been studied for 50 years because of its technological importance and fundamental interest as a model material for oxide ceramics and other refractory non-metallic substances. Despite all previous efforts, many things are still in question.

In this study, we carefully examined self-diffusion behavior in α-Al_2O_3 by means of ^{18}O and ^{26}Al tracers using TOF-SIMS. Some new insights about the mechanism of self-diffusion in α-Al_2O_3 will be proposed based on the experimental results, theoretical calculations and physical logic.

Investigation of Lithium Ion Dynamics in Copper Coated Graphite

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Graphitic materials are utilized as anode materials in most commercial lithium ion batteries. It was reported that copper coated graphite showed superior electrochemical properties compared to the pristine material.

A homogeneous coating with copper nanocrystals on a graphitic surface was obtained by the deposition of copper through a decomposition of gaseous copper formate.

Electrochemical investigation of this material gives access to lithium ion dynamics. Therefore the material is electrochemically cycled and compared to pristine graphite to see whether the electrochemical behavior is improved. The composite materials with different fractions of intercalated lithium are investigated via impedance spectroscopy. Wagner-Hebb Polarization (DC Polarization) measurements are used to separate ionic from electronic contributions to the conductivity.

A new method for the determination of effective diffusivities in inhomogeneous media

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Inhomogeneous structures can have essentially different kinetic coefficients in the subsystems. The effective diffusion permeability in the two-phase zones of the ternary systems determines the morphology of the diffusion zone as well as the growth rate of the phase layers and two-phase zones between them. Therefore, during treatment of inhomogeneous systems with noticeable volume fractions of both phases, we face the problem of ambiguity, since systems with high-conductive matrix and almost inert inclusions (and vice versa) will involve the different effective diffusivities at equal ratios of the phase volume fractions. The aim of the present study is to find a new method of definition of effective diffusivities in two-phase regions of ternary systems with the use of the Bruggemann's approach and the Kalnin's basic model for combined transition diffusion zone between two phases. It is presupposed that the effective diffusivity in a transition zone depends on diffusivities of the phases that are brought in contact, and on the additional parameter that allows general consideration of the transition zone structure. In combined model the percolation behavior of two-phase zone can be described by parameter fitting at some value of the volume fractions of phases. Calculations indicate the change of parabolic growth constant of two-phase zone. These results well match with experimental data.

Orientation dependence of ^{22}Na tracer diffusion in single-crystal Madagascar K-feldspar

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Feldspars are the most abundant minerals in the Earth's crust. Concerning their complex structure they are important for research in geology, especially for studies of the lithosphere. Diffusion processes in minerals have important applications, e.g., in radiometric dating, in geo-thermobarometry and geo-speedometry.

In this study the dependence on temperature and crystal orientation of ^{22}Na diffusion in alkali feldspar from Madagascar has been investigated by the radiotracer technique. Diffusion profiles of four different crystal orientations, i.e., perpendicular to the (001), (110), (01-1) and (010) planes, were measured at different temperatures between 773 K and 1173 K. Diffusion coefficients were calculated using the thin-film or the constant-source solution of the diffusion equation.

^{22}Na diffusion perpendicular to the (001) orientation can be fitted by the Arrhenius relation over the entire investigated temperature range yielding an activation energy of 2.01 eV and a pre-exponential factor of 3.8×10^{-2} cm^2/s. For the other orientations, i.e., perpendicular to (110), (01-1) and (010) planes, Arrhenius behavior is observed in the high temperature region between 973 K and 1173 K but upward deviations occur at lower temperatures. The slowest diffusion is observed perpendicular to the (110) plane and it is slower by a factor of 4 compared to the fastest diffusion, which takes place perpendicular to the (001) plane. At low temperatures, specifically between 773 and 873 K the anisotropy seems to disappear. The results will be compared with other diffusion data on alkali feldspars.

The effect of cyclic martensitic transformations on the diffusion properties of cobalt in Fe-18 wt.%Mn-2wt.%Si alloy

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Diffusion characteristics of cobalt in Fe-18wt.%Mn-2wt.%Si alloy after cyclic γ–ε–γ martensitic transformations were studied using the radioactive isotopes method. The observed significant increase of diffusion mobility of cobalt atoms under the cyclic γ–ε–γ martensitic transformations was due to the action of two independent mechanisms - an athermal one and a thermally activated one. The first one arose from the direct γ–ε and the reverse ε–γ transformations with corresponding direct and reverse lattice shears during alternating stresses and simultaneous lattice restructuring. The another mechanism arose under the diffusion annealing of the phase-hardened alloy. As a result of thermal cycling, defects of the crystal structure accumulated in the lattice: dislocations, low-angle subboundaries, the chaotic packaging defects, all of them being the ways of the diffusion acceleration. With increasing the degree of the phase-hardening (to 100 γ–ε–γ cycles), the penetration depth of atoms of the isotope increased twice and the diffusion coefficients after the first cycle and 100 cycles were equal 2.95×10^{-13} and 9.29×10^{-13} cm^2/s respectively.

The crystal structure defects formation in metastable alloys under the cyclic martensitic γ–ε–γ transformations and the following significant increase of the diffusion mobility of substituents at low temperatures opens up new opportunities for the creation of more intensive methods of chemical and thermal treatment. Due to the preliminary phase hardening, the temperature of the surface metallization of metastable iron-manganese alloys can be reduced by several hundred degrees.

Size Dependence of the Activation Energy of Diffusion in Multilayer Cu–Ni Films

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In this work we present the results of experimental studies of the influence of characteristic size on the diffusion rate in nanoscale Cu-Ni film systems.

The choice of this system has been specified by the fact, that copper and nickel exhibit unlimited mutual solubility in the liquid and solid states. The layered film systems were prepared by means of successive condensation of Cu and Ni from independent sources in vacuum. The mass thickness of each layer was varied in 5-100 nm range. The mass ratio of the components in the film system was equal to unity.

The methods of electrical resistance measurement during thermal cycles and in situ TEM heating were used as an experimental basis for the investigation. These techniques enable us to register onset and termination temperatures of the homogenisation process in the system under study and, thereby, to determine the activation energy of the processes being occurred.

It has been shown that the activation energy of grain-boundary diffusion decreases with system's characteristic size and amounts to 0.25 eV for the system with characteristic size of 5 nm, which corresponds to an increase in the grain-boundary diffusion coefficient by 10 orders of magnitude compared to massive samples.

Self-Diffusion in Lithium Niobate at High Temperatures

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The production of $LiNbO_3$ based components as well as the increasing application of lithium niobate at high temperatures require an understanding of the atomic transport of the constituents and of defect thermodynamics. We review the published data and compare them to our own recent results on the diffusivities of the three host elements, which were obtained using SIMS based tracer methods. Lithium is confirmed to be the most mobile species. From the lithium and oxygen diffusion data one must conclude that lithium is about 4-5 orders of magnitude more mobile than oxygen in the temperature range $800\ °C \le T \le 1100\ °C$, regardless of the exact Li_2O/Nb_2O_5 ratio.

Regarding the niobium diffusion there are only three very old data sets available published in 1975 and 1976, which are not at all in agreement. Because of the lack of a rare stable Nb tracer isotope we used Ta as a tracer to probe the self-diffusion of Nb in a VTE processed $LiNbO_3$ single crystal with nearly stoichiometric composition: (49.9 ± 0.1) mol % Li_2O. The VTE conditions were maintained during the diffusion anneal ($1000\ °C \le T \le 1100\ °C$) under a constant oxygen partial pressure of 200 mbar. The obtained tantalum (niobium) diffusivity is much lower than the values given in the literature. The discrepancies between our results and the literature data for oxygen and niobium can be consistently rationalized if the experimental procedures of the earlier works are carefully analysed – especially with respect to the most probable point defect equilibria.

The peculiarities of interaction between Ga contained solutions and polycrystalline Al

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In the scientific literature, the embrittlement phenomena and metal alloys under the action of melts under tensile stress are intensively studied. However, until now there is no proper explanation of this phenomenon, despite of decades of relevant studies. As in many other systems, where a solid polycrystalline metal, aluminum, is in contact with a liquid metal, gallium, then under certain loads brittle fracture is observed along grain boundaries. However, there are significant differences between the Al-Ga system and others. First, this effect is observed at all temperatures of the existence of liquid gallium. Secondly, the gallium-aluminum system reveals brittle fracture along grain boundary regions where gallium has penetrated. Third, and perhaps most interesting difference, the rate of penetration of gallium along the grain boundaries in Al is tens of microns per second even in the absence of external tensile stress.

The general solution of backward diffusion equation

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The diffusion is elementary and universal process in nature. The rate law of diffusion had been formulated by A. Fick in which the diffusion flux is proportional to the gradient of the concentration and diffusion flux goes from regions of higher concentration to regions of lower concentration. If the thermal velocity of molecules in lower concentration area is greater than velocity of molecules in higher concentration area, there are two molecule fluxes, one of them is the advection flux and the other is backward diffusion flux. Both the advection flux and the backward diffusion flux are going from regions of lower concentration to regions of higher concentration (backward diffusion process). The backward diffusion process is contrary to the fundamental laws of diffusion as Fick's law and Onsager's laws, but which are explained. Moreover, the equation of backward diffusion and the solution of which are also presented and discussed.

Investigation of effect of Al doping and anisotropy of oxygen diffusivity in zinc oxide

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Zinc oxide (ZnO) is a functional metal oxide that is useful in many optical and electronic applications [1]. For controlling its properties, it is important to understand the defect chemistry in ZnO. Previous studies investigated their oxygen (O) diffusivity in ZnO to obtain direct information of native defects of O sites [2, 3]. Although O diffusivity in ZnO is affected by dopants or impurity, such as Al [2, 3], the diffusion mechanism is not well understood. Moreover, anisotropy of O diffusivity in ZnO has been suggested [4] however, it also is unclear. In this study, we carried out diffusion experiment on single-crystal and polycrystalline ZnO to study anisotropy and effect of Al doping of their O diffusivity. As a result, we revealed that O diffusivity of ZnO is enhanced with increase in Al concentration in ZnO lattice. We will also report result of investigation on anisotropy of O diffusivity in ZnO and discuss defect chemistry in ZnO.

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Visualization of Li-ions diffusional behavior in solid electrolyte for lithium rechargeable battery

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Recently, all solid state LIB becomes of increasing importance to secure the safety of the LIB. In order to realize the solid state LIB, many issues have to be overcome, i.e. lifetime. Information of Li diffusional behavior in solid electrolyte serves as the initial step toward resolution of issues. For this purpose, we are proposing a visualization method using stable Li-isotope. In this paper, we will report methodological aspect using a secondary mass spectrometer, specimen preparation, and some results.

Theoretical evaluation of anisotropic distortion associated with point defects in ordered compounds

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Mechanical relaxation effects caused by stress-induced reorientation of anisotropic point defects provide a useful means to investigating elementary processes of diffusion in solids. The Snoek relaxation and the Zener relaxation are well-known examples, which are due to interstitial and substitutional solute atoms, respectively, in solid-solution alloys. In crystals of ordered structures, intrinsic point defects may cause similar relaxation effects, if the position of the defect is lower in point symmetry than the host crystal. The well-defined relaxation maximum observed in Ni_3Al could originate from either antisite Al atoms or Ni vacancies in the Ni sublattice [Numakura et al., Philos. Mag. A 79 (1999), 943]. Experimental results on Ni_3Al and Ni_3Ga [Mater. Sci. Eng. A 442 (2006), 59; ibid. 521 (2009), 34] suggest that the defects responsible for the effect is antisite atoms of the minority species. In the present work, we have examined the anisotropic distortion produced by a single point defect in the compounds of the $L1_2$ structure by ab initio calculations. Together with theoretically determined energies of formation and migration, we discuss the mechanism of the relaxation effect quantitatively and identify the responsible defect species.

Structural changes in steel 20 under ultrasonic treatment in a constant magnetic field

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The material structure evolution under ultrasonic treatment (UST) in a constant magnetic field (CMF) is of scientific and practical interest. The present work is focused on the investigation of the influence of ultrasonic treatment in a constant magnetic field on the structural changes and the rate of diffusion penetration of the ^{63}Ni isotope into steel 20.

The object of investigation is a low-carbon steel 20 (the ferrite class, 0.2 at.% C). The samples represent the cylinders of 10×10 mm size. An ultrasonic treatment of steel 20 in a constant magnetic field was performed using a special equipment (the processing parameters are: amplitude of the oscillations, ε = 10 μm, the oscillation frequency, υ = 18 kHz, the magnitude of magnetic field, H = 585 E, the direct current, I = 9 A, the processing time τ = 6102 s, and the processing temperature, T = 293 K). The ^{63}Ni isotope distribution in the steel 20 after processing was measured and the mass-transfer coefficient, D_m, was determined used the layer sectioning method and Gruzin's technique.

A metallographic examination of the initial material revealed a ferrite-perllite structure (with ~85% of ferrite and remaining perllite) and the average size of the grains was 28 μm. UST in CMF increases both the grain arrangement and the grain size, to 31 μm. The microhardness of the perllite and ferrite grains in the initial states was 1.9 GPa and 1.4 GPa, respectively. After processing, the microhardness of ferrite grains drops to 1 GPa and perllite is dissolved.

The ultrasonic treatment of steel 20 in a constant magnetic field leads to reduction of the microhardness and of the dislocation density by 60% and 72%, respectively. The X-ray diffraction examination reveals an increase (by 65%) of the residual stresses in the steel 20 after processing. This phenomenon is obvious to be caused by the point defects' creation.

The penetration depth of the ^{63}Ni tracer atoms in the steel 20 amounts to 11 μm and the mass-transfer coefficient is $D_m = 7.4 \cdot 10^{-11}$ cm^2/s. The determined D_m value coincides by an order of magnitude with the mass-transfer coefficient of Cr in Fe under the ultrasonic treatment with the frequency of 20 kHz. Thus, the ultrasonic treatment of the steel 20 performed at room temperature in a constant magnetic field doesn't substantially modify the structure state. The processing of the steel 20 is established to lead to a reduction of the ferrite microhardness and of the dislocation density and to an increase of the residual stresses in the metal lattice.

Tracking down fast Li ions in composites of ionic liquids (EMIMTFSI) and Li salts (LiTFSI) by long-time ^{7}Li NMR spin-lattice relaxation

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Novel electrolyte systems have received increased attention in lithium-ion battery research. The mixture of an ionic liquid with a lithium salt represents a conceptually new class of electrolyte materials for high-temperature lithium batteries, termed “ionic liquid-in-salt”. Here, we used ^{7}Li NMR to study both local electronic structures and Li+ self-diffusion in LiTFSI and $Li_xEMIM_{1-x}TFSI$ with $x = 0.9$. The NMR spectra, recorded under static conditions, perfectly agree with the results from differential scanning calorimetry. Upon heating to 513 K they clearly reveal several double phase regions; the known solid-state phase transformation of LiTFSI can be well recognized by the change of the quadruple powder pattern of the ^{7}Li NMR spectra of LiTFSI. A rapid increase in long-range ion conductivity, within two orders of magnitudes, takes place when the 1/2 EMIMTFSI/LiTFSI phase starts to melt. This can also be monitored by temperature-variable ^{7}Li spin-lattice relaxation (SLR) NMR. If recorded up to delay times of 1000 s, the pronounced bi-exponential ^{7}Li SLR NMR transients directly reveal a subset of highly mobile Li ions, partly identified as $[Li(TFSI)_2]^-$, which can be well discriminated from the response of pure LiTFSI. This sub-ensemble is regarded to be responsible for the enhancement in ion conductivity.

Influence of substrate temperature on mass-transfer of ^{63}Ni in Fe and Cu under electro-spark alloying

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In this work, the mass-transfer of Ni in Fe and Cu under electro-spark alloying at 77 K and 293 K is investigated by radioactive tracer method (^{63}Ni). The concentration profiles of ^{63}Ni in both Fe and Cu are found to follow the Gaussian solution. This fact is confirmed by the linear character of lg$C$ vs. x^2 dependence with x being the penetration depth. This result verifies a volume-diffusion mechanism of the mass-transfer process.

The mass-transfer coefficients, D_m, of ^{63}Ni in Fe and Cu are estimated and the mobility of Ni atoms in Cu is higher than that in Fe by a factor of 50 at 77 K. With increasing temperature the relation is reversed and ^{63}Ni becomes to be faster in Fe than in Cu by a factor of 1.4 at 293 K. The total penetration depth of ^{63}Ni atoms in Cu under electro-spark alloying at 77 K is almost fivefold of that in Fe, 70 and 14 μm, respectively.

These results can be explained by the difference of the thermal conductivities of Cu and Fe which are 1.14 cm^2/s and 0.22 cm^2/s, respectively, and their ratio is 5.19.

Hollowing of Ag-Au core-shell nanoparticles by grain boundary diffusion

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Hollow metallic nanoparticles attract great deal of attention due to their possible applications in various fields of nanotechnology (drug delivery, energy production and storage, catalysis, etc.). These particles have been s fabricated in the past employing wet chemistry methods or/and Kirkendall effect during bulk interdiffusion in the core-shell nanoparticles. The latter process requires relatively high temperatures at which the bulk diffusion is active. In this work we present a method of fabricating of the hollow Au nanoparticles based on grain boundary diffusion. We produced an array of single crystal Ag nanoparticles on sapphire employing the solid state dewetting process of a thin Ag film deposited on sapphire substrate. A thin Au film was then deposited on the dewetted sample. The Au film was heteroepitaxial on Ag nanoparticles, and polycrystalline on exposed sapphire substrate. During subsequent heat treatment at 170°C the Ag atoms from the core of the core-shell Ag-Au nanoparticles diffused along the grain boundaries of Au film, leaving behind hollow Au nanoparticles. The hollowing process and its kinetics were studied by scanning electron microscopy and by a combination of focused ion beam with transmission electron microscopy.

In situ TEM investigation of the kinetics of homogenization in Ag–Pd film system

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It is known that the diffusion processes are considerably accelerated in nanoscaled systems. Unfortunately, there is the lack of quantitative data on the activation energies and diffusion coefficients due to the complexity of experimental investigation and a plenty of factors affecting the kinetics of reaction in such systems. The aim of current work was to study the kinetics of the formation of a homogeneous solid solution in an Ag–Pd layered system by means of in situ TEM heating technique.

The layered film systems were prepared by means of successive condensation of the components from independent sources in vacuum. The lattice parameters of silver and palladium are significantly different from each other, enabling us to reliably trace a state of the system by means of diffraction methods.

It has been shown that the diffusion processes in thick Ag–Pd layered film with a grain size of 5–10nm are activated in the 453–623K temperature range. In situ TEM studies reveal that complete homogenization in fine-grained Ag-Pd film occurs with the absence of significant microstructural changes in the film system. The effective diffusion coefficient was also measured as 10^{-17}–10^{-18} m^2/s at 553K. Possible mechanism of homogenisation is discussed.

Profile of heat transfer between two different materials

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In this article we made a study on the transfer of heat in two different materials such as steel and copper. Initially we present the profile of heat transfer in each material alone, after we present the profile of the same phenomena in the two materials in contacts, and to see how the temperature is propagated when we have a variation of thermal conductivity.

The simulation is made by ANSYS software which permits us to solve the energy equation by finite element method.

Numerical Modelling of Heterodiffusion from the Variable Type Source

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In real conditions in the case of a limited solubility, diffusion from a thin film in a substrate material (matrix of diffusion) is carried out in some stages in a way that the diffusion source is gradually transformed from the "constant" source of diffusion to «infinitely thin» type of diffusion source through intermediate stages.

Numerical modeling of diffusion of an impurity from a finite-thickness layer at the presence of the limited solubility in a matrix in view of the concentration dependence of diffusion coefficient is performed. The modeling algorithm resides on a comparison of the average layer contamination during any moment of time with the solubility limit at the given temperature. The concentration distributions of an impurity in a solvent matrix at any time stage of diffusion experiment are received.

Results have shown that at average times of diffusion the concentration curves essentially differ from analytical predictions for ideal «constant» type source and «infinitely thin» layer type source. Numerical modeling allows operatively establishing the type of an operating diffusion source, to estimate a role of the concentration dependence of diffusion coefficient.

Lithium self-diffusion in compounds of the system Li_2O-Nb_2O_3

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Investigation of lithium self-diffusion in lithium containing solids is a very interesting task for the design of possible solid ion conductors. In the system Li_2O-Nb_2O_3 we choose as model systems $LiNbO_3$ which is stable over a wide solid solution range and Li_3NbO_4 the stable phase in the system with the highest lithium content.We made comprehensive studies on LiNbO3 single crystals with different Li concentration in the solid solution range and in amorphous $LiNbO_3$ in order to identify which kind of disorder (defect disorder or structural disorder) has the main influence on lithium diffusivity. For comparison we investigated also Li_3NbO_4 to find out how a higher lithium content and a different crystal structure influences self-diffusion. The measurements were carried out using secondary ion mass spectrometry. As a tracer source, thin layers of isotope enriched $^6LiNbO_3$ were deposited by ion beam sputtering on $LiNbO_3$ or Li_3NbO_4 samples. Diffusion annealing was done between 150 and 500°C.

As a result, it is found that Li diffusivities increase by at least eight orders of magnitude if structural disorder is introduced (amorphous samples). Concerning defect disorder in the $LiNbO_3$ single crystals it is found that congruent crystals show diffusivities about one order of magnitude higher than near stoichiometric crystals.

Correlation between site-energies and jump-frequencies of Cd-solutes in a series of intermetallics

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Measurements were made on rare-earth (R) palladium phases Pd_3R having $L1_2$ crystal structure of nuclear quadrupole interactions at Cd-solute atoms, using the method of perturbed angular correlation (PAC). Cd-solutes invariably occupied R-sites in samples made to have the R-poor boundary composition, as expected according to a heuristic rule that dilute impurities occupy the sublattice of the element in which there is a deficiency of atoms. For Pd-poor samples with $R =$ Lu, Yb, Er, and Tb, solutes occupied only Pd-sites at all temperatures, also as expected according to the heuristic rule, and jump-frequencies were unmeasurably small. However, jump-frequencies increased dramatically for Pd-poor alloys with $R =$ Eu, Sm, Nd, Pr and Ce. At the same time, changes of site fractions of solutes on Pd- and R-sites with temperature showed that the Pd-site is the stable site at low-temperature for Cd-solutes in Eu and Sm phases, whereas the R-site is preferred in Nd, Pr and Ce phases. Thus, the increase in jump-frequency is correlated with a "switch" in preferred lattice location of the solute. Additional diffusion mechanisms appear to become available for solute atoms that have an ambiguous site preference. Such considerations may be generally important in understanding impurity diffusion in other compounds.

Diffusion and solid state reactions in Pd-Cu thin film systems at low temperatures

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Diffusion and solid state reactions were investigated in Pd-Cu nanocrystalline films by means of SNMS (Secondary Neutral Mass Spectrometry) depth profiling technique. The heat treatments were made at such low temperatures where the volume diffusion was frozen in (150°C-310°C). First there is a grain boundary interdiffusion. In the Pd layer, from the evolution of C-type depth profiles, the Cu grain boundary diffusion coefficients were calculated at different temperatures. At longer times first a Pd plateau developed inside the Cu. Later on the Cu penetration was also more and more extended in the Pd, even the average composition of Cu in Pd becomes higher than the average Pd composition in Cu. Depending on the ratio of the initial thicknesses, the system arrived either at almost homogeneous CuPd or Cu_3Pd phase, by grain boundary diffusion induced solid state reaction (GBDIREAC). Using a simple model, assuming that the reaction layer forms at grain boundaries and grows by interface motion perpendicular to it, the interface velocity in the Cu layers was estimated from the linear increase of the average composition of Pd and its value is about 0.1 nm/h at 220°C.

MD-simulation of the contact metastable melting process in Ni-Al system

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SHS reaction in the Ni-Al multilayers depends on the conditions of preparation and aging of foils. Numerical study of SHS in Ni/Al foils, taking into account the formation of preexisting phase layers, was conducted, for example, by Weihs et al., F.Baras and O.Politano studied the reaction for the case when the preexisting layer of the intermediate phase had not been formed during deposition and subsequent storage. They demonstrated that in this case the ignition could lead to disordered phase formation, which was treated as amorphous phase. We suggest (after discussions with Baras and Politano) that mentioned disordered phase is actually a liquid solution of Ni in Al. In fast SHS process, the intermetallic phases may have no time for nucleation or they can be kinetically suppressed by the fast growing disordered phase. In this case, one should consider the metastable system containing only solid and liquid solutions of Ni in Al and vice versa.

We suggested that the penetration of Ni into Al leads to decrease of both solidus and liquidus. This hypothesis was recently checked by CALPHAD-based construction of metastable phase diagram for Ni-Al. We tried checking of the contact melting hypothesis by MD-simulation of Ni-Al contact reaction and measuring the tracer diffusion coefficients within inner layer. Also the sample of Ni-Al alloy with a predetermined concentration and random spatial distribution of atoms of each sort over lattice sites is simulated, then the system is heated with monitoring of its melting. Lowering of the melting temperature with rising nickel content was established.

Phenomenological study of phase competition at the initial stage of Ni-Al reaction

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Nickel-aluminum system has been studied for a long time and is widely known due to applications of high-temperature phase Ni-Al by and super-alloys based on the Ni_3Al-phase. Now Ni-Al system is widely used for SHS reactions in the multilayered foils. Usually the $NiAl_3$ phase is considered as the first phase to grow in this system. Yet, there are some papers indication the NiAl as the first phase to form. Moreover, recently F. Baras and O. Politano studied Ni-Al reaction by MD-study and found some disordered phase as a first phase to grow. The following results of a phenomenological modeling of nucleation and reactions at the initial stages are presented:

- A metastable phase diagram Ni-Al in the absence of intermetallic phases (assuming their kinetic suppression) has been built;
- The possibility of contact melting at the interface of the solid nickel and aluminum above the temperature 695 K is predicted;
- The kinetics of the of the liquid Ni-Al layer growth till the full consumption of aluminum layer is described;
- The nucleation of one of intermetallic phases at the interface Ni/melt by precipitation from the supersaturated melt is discussed;
- The obtained results are analyzed within the theories of nucleation in the concentration gradient and of the Flux Driven Nucleation.

MD study of deposition conditions effect on phase competition in Ni-Al reaction

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As was shown recently by MD experiments (F.Baras and O.Politano), direct contact of the single crystalline Ni and Al can lead to disordered layer as a first phase to grow. There is reason to suppose that this disordered phase can be a liquid one. However, if preceding preparation of a multilayer led to the formation of some compounds at the interface between Ni and Al, the path of phase evolution may significantly change. If the contact melting does not happen, then the nucleation barriers, mobilities and the formation sequence will be completely different. Therefore we studied the structures arising during deposition of Ni over Al and vice versa, depending on the flux density and temperature. At that, we used the MD simulations with EAM potential.

Main results:

- If the deposition flux density is low enough and the total flux is large enough, then the partial ordering takes place at the interface.
- After some initial period a new BCC phase starts forming in the contact zone during the deposition.
- Dependencies of the number of atoms belonging to the newly formed phase with BCC lattice on temperature and flux density, were measured.
- The contact melting during deposition occurs under melting temperature of Al.

Diffusion homogenization in Pt/Fe/Ag/Pt and Fe/Ag/Pt thin-film systems

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Pt(2nm)/Fe(15nm)/Ag(10nm)/Pt(15nm)/SiO_2 and Fe(15nm)/Ag(10nm)/Pt(15nm)/SiO_2 (Group I) as well as $Fe_{50}Pt_{50}$(15nm)/Ag(7,5nm)/SiO_2 (Group II) thin films were investigated by secondary neutral mass spectrometry. Isotherm annealing of samples of Group I was carried out between 245°C and 390°C. Isochrone (30 s) heat treatments of both groups were carried out between 600°C and 900°C (in 100°C steps). In films of Group I first there is a strong intermixing between Ag and Pt, resulting in formation of Ag_xPt_{1-x}. The processes are much faster in the Ag-layer with segregation of Ag to the substrate/Pt interface. Later on the Pt starts to penetrate to the Fe grain boundaries leading to the formation of FePt. At the same time the Pt even leaves the PtAg phase, thus the Ag layer "moves" to the substrate. Finally a fully homogeneous FePt phase has been formed, without considerable intermixing between the FePt and Ag. Rapid thermal annealing in samples of group II resulted in formation of homogeneous ordered FePt with randomly distributed Ag (and Ag segregation at the top of FePt). Taking into account the strong segregation tendency of Ag the uniform Ag distribution can be explained by Ag segregation/precipitation along grain boundaries, which is desirable for improved magnetic properties.

The Model of the Layer Boundary Diffusion in Multilayer Materials

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The results of metallographic studies show the effect of the layers thickness of multilayer metal material on the diffusion depth after chemical heat treatment. The accelerate diffusion model of diffusible element along layers boundaries is proposed.

Diffusion behavior of sodium in polycrystalline Cu(In,Ga)Se_2 layers

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Polycrystalline thin film Cu(In,Ga)Se_2 (CIGS) solar cells require a sufficient amount of sodium (Na) to be highly efficient. To insert Na systematically into the CIGS absorber it is helpful to know the diffusivity of Na in CIGS and which diffusion mechanism occurs. Therefore the sodium diffusion in CIGS layers was investigated over a temperature range from 157°C to 400°C. The diffusion profiles were measured by secondary ion mass spectrometry (SIMS). Sodium ions diffused from a sodium fluoride (NaF) layer on the CIGS surface into the CIGS layer. From Na diffusion profiles, the diffusion along grain boundaries (GB) could be distinguished from the diffusion into the grain interior (GI). Atom-probe tomography measurements reveal that even at a low temperature of 157°C bulk diffusion of sodium into CIGS occurs. Based on this data, the slower diffusion coefficient in the volume can be described by the Arrhenius equation = 9.7×10^{-9} exp (-0.36 eV$/k_B T$) cm^2s^{-1} and the fast diffusion along the grain boundaries by = 6.5×10^{-9} exp (-0.21 eV$/k_B T$) cm^2s^{-1}. Hence, we propose that sodium ions do not only passivate grain boundaries, but also act as dopants in the CIGS bulk.

Observation of oxygen diffusivity in perovskite oxides by impedance and mechanical spectroscopy

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Perovskite-type oxides are highly expected to be used as electrodes or electrolytes in solid oxide fuel cells because of their high ionic conductivity at elevated temperatures. Since the ionic conduction due to oxygen diffusion is mediated by oxygen vacancies, the microscopic motion of oxygen vacancies must be also understood to provide an idea on how to design materials with suitable conductivity for application. Impedance spectroscopy is usually used for the evaluation of ionic conductivity. On the other hand, mechanical spectroscopy is a useful tool for obtaining the microscopic information on the motion and concentration of point defects if the defects induce anelastic relaxation due to the stress-induced redistribution; oxygen vacancies in perovskite oxides with cubic unit cells are expected to exhibit such anelastic relaxation. In this study, oxygen diffusion in $Ba_{0.5}Sr_{0.5}TiO_3$ and $SrTiO_3$ has been studied by the combination of impedance and mechanical spectroscopy.

About the formation of the supersaturated solid solutions by diffusion process

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It is generally agreed that in conditions of thermodynamique equilibrium at interfaces, the supersaturated solid solutions cannot be formed by diffusion. Nevertheless, in many cases the formation of equilibrium phases is made difficult due to kinetic and other reasons. The formation of metastable phases (e.g. supersaturated solutions) becomes possible.

The analysis is performed of the concentration profiles for bulk diffusion obtained at low temperatures consistent with B-regime for grain boundary diffusion in systems Cu/Al, Fe,Co/Cu.

It is shown that in these systems the supersaturated solutions are formed and the extent of supersaturation is the more as the diffusion temperature is lower. The concentration of diffusant may be 5-10 times larger than the solubility according to phase diagram.

Time dependence of interdiffusion coefficients determined from thin film diffusion couples

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Recently the diffusion intermixing in thin film couples can be investigated employing high resolution profiling techniques. The published unexpectedly low activation energies and frequently time dependent diffusion coefficients indicate that grain boundary and other short circuit contributions during intermixing may play important roles. We developed a simple numerical model which is suitable to calculate the average concentration vs. depth function in an A/B isotope polycrystalline bilayer sample. In the model we supposed regularly spaced parallel grain boundaries which are perpendicular to the original interface. Since the experimental methods evaluate the effective diffusion coefficient from the concentration gradient detected at the original interface, we evaluated the same parameter using our model. Our results demonstrate that the 'centre gradient' evaluation method at small bulk penetration depths (Harrison type C-regime) gives time dependent diffusion coefficients. The intermixing can be divided into three stages:

i) filling the grain boundaries (grain boundary diffusion control),
ii) practically there is no change in the gradient (still there is no bulk penetration yet, but the grain boundaries already filled),
iii) the intermixing is controlled by bulk diffusion if the condition of the type B regime is fulfilled.

Theoretical model for Ge condensation under SiGe oxidization

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The so-called, Ge-condensation technique, is a promising way to realize thin Ge layers of good quality for high mobility MOSFET channel. In this context, oxidization of a dilute Si(Ge) alloy is modeled using an original protocol based on molecular dynamics simulation and rules for the oxygen insertions. These rules, deduced from ab-initio calculations, favor the formation of SiO_2 against GeO_2 oxide which leads to segregation of Ge atoms into the alloy during the oxidization front advance. Ge condensation is then observed close to the SiO_2/Ge interface due to the strain induced by oxidization in this region. From the analysis of the simulations process, we propose a one-dimensional description of Ge condensation which perfectly reproduces the evolution of the Ge concentration during oxidization of the SiGe alloy.

Observation of Si self-diffusion enhanced by the strain originated from end-of-range defects using isotope multilayers

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We investigated Si self-diffusion enhanced by end-of-range (EOR) defects using Si isotope multilayers grown by solid source molecular beam epitaxy. The structure is composed of seventeen 10-nm-thick isotopically pure ^{28}Si layers, which are separated from each other by a 10-nm-thick natural Si layer. Si self-diffusion is investigated through the ^{30}Si diffusion. The isotope multilayers were amorphized by 150keV Ge^{+} ions with a dose of 2×10^{15} cm^{-2} at room temperature and annealed at 800-1000°C. After annealing, the samples observed in cross-sectional transmission electron microscopy show EOR defects just beneath the former crystalline/amorphous interface at a depth of about 175 nm. The samples without implantation were also annealed as a reference to observe the thermal equilibrium diffusion. The experimental result of secondary ion mass spectrometry shows transient enhanced diffusion (TED) by excess self-interstitials (I's) generated from {311} I clusters and EOR defects, which can be explained by the previous TED models. In addition, we found further enhancement of Si self-diffusion at the EOR defect region. This additional enhanced diffusion indicates the existence of tensile strain at the EOR defect region because TED is governed by I supersaturation and I-assisted diffusion is known to be enhance by tensile strain.

Distribution of permeation rates through nanopores

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We study the permeation of polymers through nanoporous walls of polymer capsules. These are prepared via Layer-by-Layer coating of silica particles, where core dissolution causes a porous wall. The distributions of pore number and size are available from high resolution scanning electron microscopy.

The main focus of this study is the exchange process between free polymers in dispersion and encapsulated chains. With diffusion experiments (Pulsed Field Gradient NMR) we distinguish polymers in either site by their respective diffusion coefficients. This exchange system can be described by a two-site model. Variation of the observation time in the regime of intermediate exchange yields the exchange time of chains through pores.

The distribution of pore sizes is expected to cause a distribution of exchange times, which we describe for the first time by varying the observation time window. With this method, we are able to study the dependence of permeation on the chain length and architecture (linear and star polymers). The results show that for short chains the permeation process is diffusion controlled. For long chains, measured with non equilibrium diffusion experiments, we obtain a different mechanism.

Ion diffusion in gel polymer electrolytes

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Lithium ion containing polymer electrolytes, based on mixtures of polymer, lithium salts and ionic liquid or alkyl carbonates are potential good ion conductors for application in rechargeable lithium batteries. Mixtures of pyrrolidinium based ionic liquids, organic carbonates and lithium imide compounds are described in literature because of their excellent electrochemical properties regarding energy materials. The main constraint in this field is ionic cluster formation of lithium cations with fluorinated anions. In contrast to conductivity experiments, Pulsed Field Gradient NMR diffusion experiments have the advantage of giving element specific diffusion coefficients. Here, we study the lithium and fluorine diffusion in gel polymer electrolytes of different compositions. However, we are investigating the effectiveness of the polymer backbone to mobilize the lithium ion from anionic clusters. We compare both charged and neutral polymers to form the polymer electrolyte gels and study the diffusion of the cation in presence of the ionic liquids or organic carbonates.

In our study, mixtures of lithum bis(trifluoromethanesulfonyl)imide, polymethyl methacrylate or poly(diallydimethylammonium bis(trifluoromethanesulfonyl)imide) and organic carbonates, are investigated as feasible gel electrolyte to study the ionic diffusivity in the homogeneous medium. NMR diffusion and conductivity experiments reveals insight into the ion (lithium) transport in the gel electrolytes.

Radiotracer measurements of Na diffusion in Cu(In,Ga)Se2 thin films

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Na is an important impurity in solar-grade Cu(In,Ga)Se_2 (CIGSe) as it improves the light-conversion efficiency in photovoltaic applications. In standard fabrication processes running near 600°C, Na diffuses from the soda-lime glass substrate through the Mo contact layer into the active zone of the solar-cell structure. However, dedicated Na diffusion experiments are difficult to perform, which has led to a lack of reliable data and to poor knowledge about the diffusion mechanism. We investigated Na diffusion with the radiotracer technique using a ^{22}Na source deposited at the CIGSe front surface. It is remarkable that the depth profiles resulting after diffusion in a lamp oven and subsequent sectioning by ion-beam sputtering exhibit peculiar shapes. Obviously, the observed behaviour is strongly affected by the absorption of Na in glass substrate and layer interfaces. Our findings point to the simultaneous occurrence of a fast and a slowly moving Na species. It is shown that the diffusivity assessed for the slow Na species is in fair agreement with the redistribution of ^{23}Na during the diffusion of natural Fe into CIGSe, as deduced from SIMS depth profiling.

Influence of beryllium content on the interaction in the system U-Mo/Al-Be

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Currently, the majority of research work on nuclear reactors nuclear dispersion fuel, represents a mixture of spherical particles of alloys or compounds of uranium in a matrix of material having high thermal conductivity, such as aluminum.

The uranium-molybdenum alloys have best performance characteristics. There a problem of interaction between aluminium matrix alloy and U-Mo fuel particles. In the result the formed intermetallic layer is not stable under irradiation and leads to a catastrophic swelling and early fuel rods failure.

In this work, we studied the effect of beryllium doping on the kinetics of formation interaction layer in UMo / Al. It is shown that aluminum beryllium doping significantly increases its compatibility with UMo alloys.

Chemical diffusion in eutectic liquid Al-Cu-Ag and its binary constituents

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Chemical diffusion coefficients for eutectic E1 Al-Cu-Ag and its binary constituents are presented in the liquid phase. Complementary methods like in-situ X-ray and neutron radiography as well as ex-situ shear-cell techniques have been employed for the chemical diffusion coefficient measurements. The binary data are supplemented by self-diffusion data determined by quasielastic neutron scattering. These data are discussed in the framework of the Darken relation. For $Al_{80}Ag_{20}$ [at. %] it is demonstrated that the Darken relation predicts chemical diffusion within 15 %. For the ternary system, the full diffusion matrix is determined. To this end, three diffusion couples with one element set as constant and three diffusion couples with variable concentrations of all three elements have been processed.

As a result, it is proved that uphill diffusion is not present for the eutectic E1 and therefore a quasi-binary analysis of the experimental results is justified. Further it is shown that within the experimental error of 15 % all chemical diffusion coefficients in the liquid were equal.

Mechanism for the Electromigration of Ag-alloy wires with various Pd and Au contents

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An innovative Ag-Au-Pd alloy wire has been developed for the substitution of traditional Au wire and Pd coated Cu wire in electronic packages. In this study, the mechanism for the electromigration of such Ag-alloy wires containing different amounts of Pd and Au has been studied. Morphology of the cross sections indicated that a thinning and thickening phenomena accompanying the grain growth appeared in the worn-out alloy wires after the current stressing. The mean time to failure (MTF) of these Ag-alloy wires stressed with various current densities depends strongly on their electrical resistivity, which leads to the increase of wire temperature during current stressing due to the Joule effect. With kinetics analysis, the activation energies for electromigration show a contrary tendency with those for atomic diffusion in the Ag-alloy wires. Summarizing the experimental results, a failure mode for such an Ag-Au-Pd alloy wire under current stressing has been concluded to depend on the current density (J) and the activation energy (Q) from the kinetics' analysis as: $MTF^{-1} = (A/\pi r^2)\, J^2 \exp(-Q/kT)$.

Improved compatibility of steels with metallic nuclear fuel at high temperatures

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Development of nuclear energy requires solving the problem of radioactive waste. One of the possible solution is the closure of the nuclear fuel cycle by using of the fast breeder reactors. However, the main problem of fast breeder reactors is high cost of fuel component (to date ceramic nuclear fuel (U,Pu)O2 is used).

It is possible to improve the economy, and safety and simplify the technology of fast breeder reactors by transition to metallic nuclear fuel based on uranium alloys. However, the main problem of this type of fuel - poor compatibility with steel at elevated temperatures (contact melting occur at 700°C).

In this paper, reactive diffusion between the U- Mo and U-Zr alloys and Fe-Cr and Fe-Cr-Al steels are investigated. It was found that the introduction of aluminum in the steel can almost completely suppress the formation of liquid phase at temperatures of 800°C.

These results allow us to start searching of optimal compositions of ferritic-martensitic steels, alloyed with aluminum, with have high compatibility with metallic nuclear fuel.

Extremely Slow Lithium Ion Diffusion in γ-$LiAlO_2$

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Li ion conductors have attracted much attention in the field of energy storage. In this work the fundamental investigation of Li diffusion processes in solids is continued. Lithium aluminate, $LiAlO_2$, has been chosen as a model substance to study Li ion motions. It is relevant for the application in the energy industry, e.g., as electrolyte additives in batteries. Additionally, $LiAlO_2$ is used as tritium breeding material in fusion reactors and as substrate for the epitactic growth of III-V semiconductors. In the latter cases the small Li diffusivity is important.

We report on impedance spectroscopy (IS) and solid state nuclear magnetic resonance (NMR) measurements of γ-$LiAlO_2$. The measurements have been carried out at high temperatures (from 300 K to 970 K) because of the very slow Li motion. For the IS measurements thin films of Pt as well as Ag paste with Pt sheets are used as electrodes. Additionally, ^{7}Li spin-lattice relaxation NMR measurements in rotating and laboratory frames of reference have been performed. Li transport was investigated both in single crystals and microcrystalline samples for comparison. With the information obtained from these measurements diffusion of lithium ions can be studied on different length and time scales.

The multiple martensitic transformations effect on diffusion of substituents in iron-based alloy

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Diffusion characteristics of iron and nickel atoms were investigated using radioactive isotopes method in phase-hardened metastable iron-nickel Fe-31.7%Ni-0.06%C alloy with nanofragmented structure. The diffusion coefficients increased and at the temperature of 400°C they corresponded to stationary diffusion coefficients at 900°C. Two factors influenced the diffusion acceleration: a three-order increase of the dislocation density that reached a value of 5×10^{11} cm^{-2}, and additional low-angle subboundaries of disoriented nanofragments with deformation twins subboundaries, formed as a result of γ–α–γ cycles. Low temperature diffusion anomaly in iron-nickel alloy after multiple γ–α–γ transformations was similar to that described in the literature diffusion abnormalities in nanocrystalline materials obtained by gas condensation method, electrodeposition method, and intensive plastic deformation.

Ionic conductivity of single-crystal alkali feldspars: dependence on composition, orientation, and temperature

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We measured the electrical conductivity of single crystals of monoclinic alkali feldspar with chemical composition $K_xNa_{1-x}AlSi_3O_8$, where $x = 0.72$ originates from Rockeskyler Kopf (West Eifel), $x = 0.85$ from Volkesfeld (East Eifel) and $x = 0.95$ from Madagascar. These three different compositions were investigated for different orientations over the temperature range from 300°C to 900°C and over the frequency range from 0.01 Hz to 13 MHz. Experimental data result from two different set-ups, each consisting of specific equipment. i.e., sample holder, high-temperature furnace, impedance analyzer, and evaluation software.

In Bode plots of the real part of the conductivity, extended DC plateaus are found at fixed temperatures. The DC conductivity exhibits Arrhenius behavior over the whole temperature range for all compositions and orientations, which enables us to determine activation energies of charge transport. We observe differences in the conductivity between different compositions. Using the Nernst-Einstein equation, the present results are compared with available diffusion data related to the alkali sublattice in alkali feldspars. Fair agreement with the Na tracer diffusivity in the same crystals is found in several cases. The results will be discussed in terms of possible defect and diffusion models.

An NMR Investigation of Low Viscous Fluids Confined in Mesoporous Systems

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Variable pressure and temperature Nuclear Magnetic Resonance (NMR) measurements were performed to study the diffusion and relaxation of low viscosity fluids (water and methanol) in the mesoporous systems of 200 nm silica (4 nm pore size) and controlled pore glass (cpg) (25 nm pore size). These systems were chosen to study dynamics effects of confined low viscosity liquids in geological systems that represent natural Earth systems. As fluid volume fraction decreased diffusion values decreased for all systems, consistent with a greater fraction of fluids confined to the pores. High pressure measurements on the confined water systems were characteristic of bulk water, implying minimal interactions with the pore walls. As expected the diffusion increased with increasing temperature in both Methanol and Water for the silica and cpg. Heating and cooling of the samples showed reproducibility for relaxation and diffusion measurements indicating that the porous systems do not undergo structural changes when heated and that the volume fraction of fluid does not change. Deuterium Spin-Lattice relaxation times were measured for both CH_3OD and CD_3OH as a function of temperature and volume fraction with the results to be presented.

Solid-state NMR studies on ion dynamics and local structure in cubic Li_xTiS_2

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Lithium titanium disulfides are attractive materials for lithium ion batteries, because of their high cyclability and lithium diffusivity. Cubic, trigonal and rhombohedral modifications of Li_xTiS_2 are the three important structure variants. The cubic polymorph was synthesized using an alternative method to that in our previous work, by the heat treatment of elemental Cu, Ti and S for several days. After oxidative extraction of Cu, chemical lithiation was done on cubic-TiS_2. Solid-state NMR relaxation experiments are used to analyze the dynamics of lithium ions in these materials with different lithium contents. NMR relaxation studies yield activation energies for the diffusion process, the jump rates and possibly the dimensionality of the diffusion pathways. The solid-state NMR experiments were done with a Bruker MSL spectrometer at a ^{7}Li Larmor frequency of 38.86 MHz. We have employed spin-lattice relaxation in the laboratory frame and rotating frame measurements at variable temperatures. In addition to this, we have carried out ^{33}S solid-state MAS NMR studies of the cubic and trigonal structures of Li_xTiS_2 at a Larmor frequency of 46.07 MHz. With evidence from the NMR measurements, the present work describes dynamics and structure differences in these materials.

Cobalt doping as the controlling factor of oxygen diffusivity variation by more than four orders of magnitude in polycrystalline ZnO

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Zinc oxide (ZnO) is a one of the most promising materials in the field of electroceramics, and is useful in many optical and electronic applications [1]. To improve its properties, several dopant such as Co and Mg oxides were added with ZnO [1, 2], however, the electrical activity the dopants is unclear. It has been known that the electrical properties of ZnO are influenced by their defect chemistry. To understand the defect chemistry in ZnO, previous studies investigated oxygen diffusion of ZnO doped with the dopants, for example Mg [3] and Al [e.g. 4]. In this study, we performed oxygen diffusion experiments on ZnO doped with Co. As a result, we revealed that increasing the Co concentration in ZnO clearly Co-doped ZnO by about four orders of magnitude above that of an un-doped sample was observed. We compared the results with previous reports of oxygen diffusivity of ZnO doped with other dopants and discuss oxygen defect chemistry in ZnO.

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Oxygen diffusion in Samarium doped $BaTiO_3$ ceramics

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Barium titanate ($BaTiO_3$) based materials are applied such as multilayer ceramic capacitors (MLCCs) and the positive temperature coefficient resistors (PTCRs). In among of dopants, rare-earth elements (REEs) are an important to apply above devices. The doping of REE into $BaTiO_3$ leads to decrease the electrical resistance and to decrease the oxygen diffusivity [1]. In order to study the oxygen defect chemistry, it is important to justify the cation ratio of A-site and B-site in this material, because the difference from A/B=1 causes the increase of oxygen vacancy concentration. In this study, we have fabricated Sm doped $BaTiO_3$ with the different A/B ratio. The oxygen diffusivity in Sm doped $BaTiO_3$ changed with the A/B ratio. So, we would like to show other results on oxygen diffusion phenomena in this materials.

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Impact and role of ZnX_2 (X= Cl, Br, I) on the Growth of Zinc-rich Layers on steel generated by Vapour Galvanising (Sherardising)

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Using a vapour galvanising technique called Sherardising we investigated the growth kinetics of zinc-iron phases on different steels [1]. In this work we focused on the impact of zinc halide added to the Sherardising process. For this purpose polished low carbon steel plates and zinc powder mixed with small amounts of ZnX_2 (X= Cl, Br, I) were sealed in quartz ampoules under inert gas atmospheres and annealed. During annealing, which was performed at different temperatures (603 – 683 K) and times (1 - 18 h), the ampoules were rotating by affixing them to a revolving engine.

Reaction between zinc and iron is mediated by the high zinc vapour pressure. Thickness and composition of the observed zinc-rich phases were studied by means of optical microscopy and scanning electron microscopy. The results are presented and discussed in the background of the type and amount of the added zinc halide. It turned out that a distinct increase in layer thickness can be achieved, when a certain quantity of ZnX_2 is added to the zinc powder.

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Ion transport in electrolytes based on a polyether matrix complexed with an ionic liquid

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Solid polymer electrolytes (SPEs) may be utilized in, e.g., batteries and dye-sensitized solar cells (DSSCs) because of their advantages with regard to liquid electrolytes. The investigated SPEs are complexes of poly(ethylene oxide) (PEO) with the ionic liquid 1-propyl-3-methyl-imidazolium iodide (PMImI) or similar complexes consisting of copolymer poly(ethylene-propylene oxide) (P(EO-PO)) and PMImI. The polyether oxygen-to-salt molar ratio was adjusted to 20 and 30 for each system. The direct-current ionic conductivity was determined by electrochemical impedance spectroscopy (EIS) between room temperature and 130°C, which includes the melting temperature (T_m) of the two different semi-crystalline polymers.

Above T_m, the conductivity increases with increasing temperature up to about 125°C in a Vogel-Tammann-Fulcher-like manner. The subsequent decrease in conductivity may be rationalized by precipitation of the ionic liquid (IL) from the electrolytes. Below Tm, consecutive heating-up and cooling-down cycles exhibit a hysteresis-like behaviour. Apparently, this relates to nucleation and growth of polymer crystallites during undercooling in conjunction with the common finding that the conductivity in the amorphous regions is much higher than in the crystalline ones.

A comparison between the two compositions shows that their temperature dependences run parallel in the fully amorphous range above T_m. The observed difference in conductivity of about 50% agrees with the difference in salt concentration. We currently investigate the effect of pure iodine addition (I2) to the polymer/IL-iodide complexes, which is relevant to their application in DSSCs. To this aim, conductivity data to be obtained by EIS will be compared with the results of current-voltage measurements to be performed on an electrochemical cell with ion-blocking electrodes.

Effect of surface roughness on depth profiling by ion-beam sputtering: Numerical simulations and tracer diffusion experiments

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It is shown by numerical simulation that surface roughness affects the measurement of diffusion profiles by means of sectioning techniques [1]. This problem arises in radiotracer diffusion studies of impurities in thin-film solar-grade $Cu(In,Ga)Se_2$, which exhibits an appreciable surface roughness of typically 100 nm due to the special manufacturing process of the polycrystalline layer structure [2,3]. We find that in unfavourable cases the experimentally determined diffusivity can be significantly higher than the true diffusion coefficient D. This discrepancy appears to increase with the ratio of the root-mean-square surface roughness R_{rms} to the average penetration depth $(2Dt)^{1/2}$ attained after a diffusion time t. It can be concluded, however, that the employed ion-beam sputtering technique, which involves rotation of the diffusion sample, usually leads to experimental errors of ~10% or less. The results of this study may be also relevant to other depth profiling techniques such as secondary ion mass spectrometry.

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Determination of the structural grain boundary width

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Grain boundaries (GBs) have a significant impact on the physical, especially mechanical properties of polycrystals. The high-angle GBs are typically characterized by structure units, which are different compared to crystalline unit cells, they possess an excess of free volume and, thus, are short-circuit diffusion paths. One of the most important characteristics is the GB width [1].

Generally, two types of GB width can be introduced, namely the "diffusional GB width" and the "structural GB width". It was established that the diffusional GB width in metals is practically independent of the temperature, material purity and the specific lattice [2] and it is about 0.5 nm on average. At the same time there is no experimental data on the temperature dependence of the structural GB width.

In the previous study we described a new approach to determine the excess free volume of a GB from high-resolution transmission electron microscopy (HRTEM) images [3]. For this purpose, an image analysis tool has been elaborated that allows determination of the differences of local mass density from HRTEM images and, using a proper averaging masks, the GB width can even be deduced.

In order to prove this concept, Al symmetrical tilt GBs with zone axes along the [100], [110] and [111] directions have been generated using molecular dynamics simulation (applying the LAMMPS software [4]). The atomic positions were subsequently taken as input for the simulation of HRTEM images using the Kirkland code [5,6].

The structural GB width, defined as the width of the area with decreased local density, is found to be (0.29 ± 0.01) nm and (0.22 ± 0.02) nm for high- and low-angle GBs, respectively. The GB width was found to increase slightly with the temperature, on about 0.04 nm as the temperature increases on 600 K.

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Diffusion and microstructure in ultrafine grained nickel

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Ultrafine grained and nanocrystalline materials produced by methods of severe plastic deformation (SPD) have roused a growing interest in science and technology. Previous experiments on SPD nickel of 99.6% purity revealed ultra-fast diffusion rates in ultrafine grained material severely deformed via equal channel angular pressing (ECAP) [1]. The present study reports the effect of pre-annealing of ECAP-processed Ni on the grain boundary characteristics and the thermal stability of microstructure. In order to analyze the impact of the strain path and particularly of the hydrostatic component of the applied stress, the same material has been applied to high pressure torsion, too (5 turns, 2 GPa applied pressure). Grain boundary self-diffusion has been measured using the ^{63}Ni radioisotope in combination with high-precision parallel grinding. The results of the diffusion measurements and of measurements by electron backscattered diffraction and transmission electron microscopy are discussed with respect to modifications of grain boundary structures under different routes of SPD processing.

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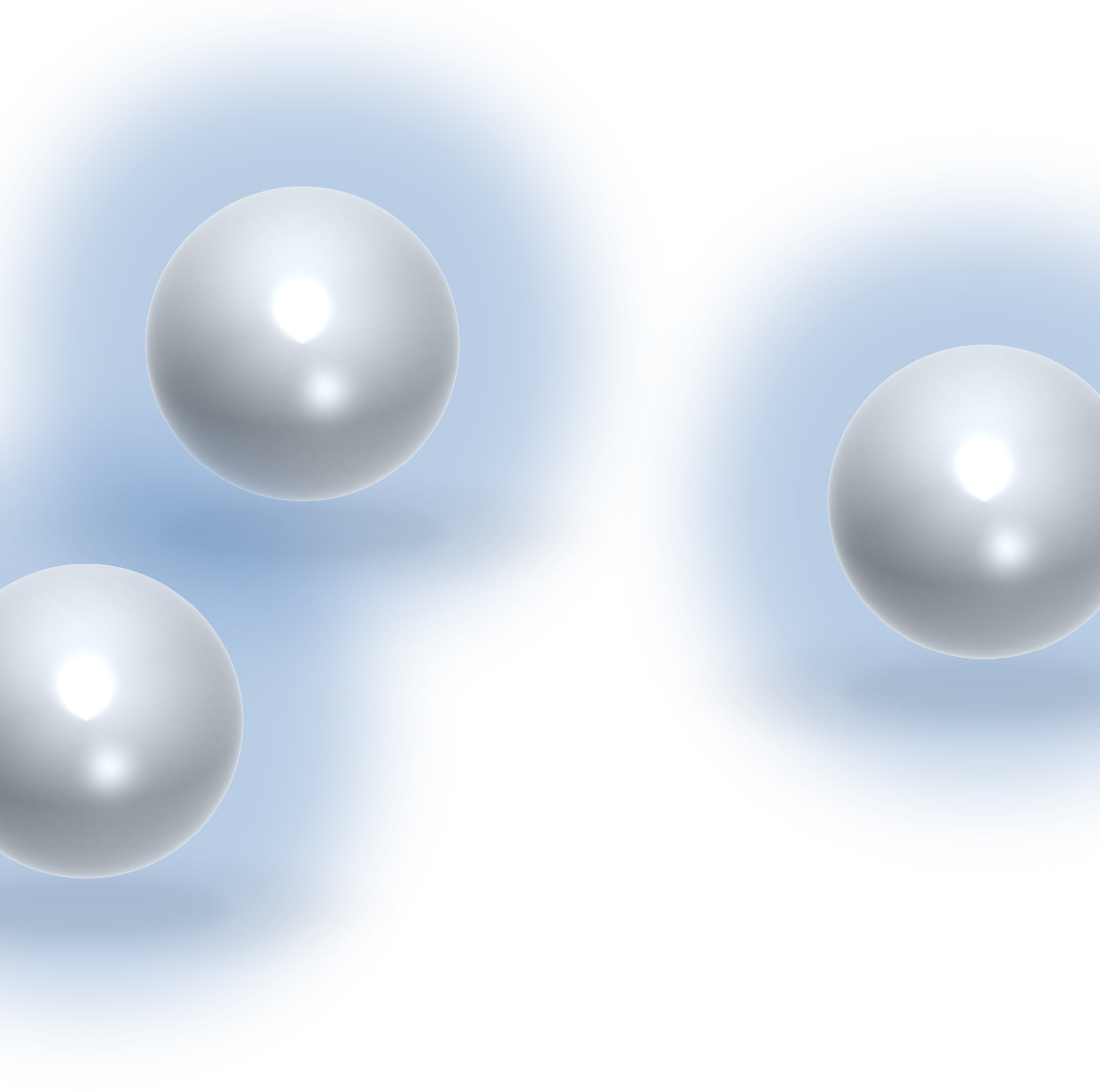

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