Diffusion in Oxides

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Diffusion processes in oxides play an important role, e.g., during solid state reactions between oxides, or for the application of oxides as functional materials such as fuel cells or oxygen permeation membranes. Defect association and trapping of defects have a strong influence on charge and mass transport in oxides, since both the Onsager transport coefficients and the thermodynamic driving forces depend on association and trapping of defects. Special emphasis will be laid on the association of defects, the off-diagonal transport coefficients, and the implications for diffusion processes. Experimentally, cation and oxygen diffusion coefficients can be determined as a function of the thermodynamic variables using either radioactive tracers or stable isotopes and secondary ion mass spectrometry (SIMS). Examples will be discussed for semiconducting oxides and oxygen ion conductors. These results will be used to explain the kinetic demixing of multicomponent oxides exposed to gradients of thermodynamic potentials (oxygen potential or electric potential) which is one basic degradation mechanism during application of such materials.

Diffusion and Ionic Transport in Borate Glasses

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The study of mobile ions in highly disordered materials addresses one of the basic questions of solid-state ionics. In addition, ion-conducting materials have high potential for electrochemical devices such as oxide fuel-cells, solid-state batteries, or chemical sensors. Network glasses are a special type of disordered structures. From the structural viewpoint alkali-borate glasses are well suited for the study of basic aspects of ionic motion in network glasses. In the recent years we have started a program, in which we investigate the ionic conduction and tracer diffusion of alkali ions in the following borate glasses: sodium borate glasses and rubidium borate glasses of various alkali contents and mixed sodium-rubidium borate glasses with several Na/(Na+Rb) fractions and of different total alkali contents. The talk will provide an overview of the experimental techniques, which include density measurements, differential scanning calorimetry, impedance spectroscopy, and tracer diffusion experiments. The results include trends in the glass-transition temperatures and in the molar volumes, which can be attributed to structural changes in the glass network. The major results concern dc electrical conductivity and tracer diffusivities as functions of temperature and composition. The dc conductivities and tracer diffusivities increase with increasing total alkali content by orders of magnitude. In the mixed-alkali system the dc conductivity has a deep minimum for intermediate Na/(Na+Rb) fractions. This minimum becomes deeper with decreasing temperature. The tracer diffusivity of Rb in the mixed glass decreases exponentially with decreasing Rb/(Na+Rb) ratio, whereas the tracer diffusivity of Na also decreases with decreasing Na/(Na +Rb) ratio on the Na-rich side, but reaches a plateau on the Rb-rich side. The lines which describe the two tracer diffusivities as functions of composition intersect near Na/(Na+Rb) = 0.2. This crossover explains the minimum in ionic conductivity and is almost independent of temperature and total alkali content.

Atomistic Modeling of Diffusion in Materials

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This talk gives an overview of the methodology, recent progress and current status of atomistic computer simulations of diffusion in crystalline materials. Several approaches are discussed, including molecular dynamics, on-the-fly Monte Carlo methods, transition state theory etc.. For ordered intermetallic compounds, understanding the underlying diffusion mechanisms is the key step of the calculations. This problem is analyzed using the NiAl, Ni_3Al and TiAl compounds as examples. It is shown that vacancy jumps in NiAl can occur by collective transitions involving two atoms, whereas diffusion in Ni_3Al and TiAl is dominated by normal nearest-neighbor jumps within and between sublattices. Examples of diffusion calculations in these intermetallics are discussed and compared with experiment. Grain and interphase boundary diffusion is another area where highly sophisticated atomistic simulations have resulted in a drastically improved understanding of diffusion mechanisms. This is illustrated by recent simulation results for self- and impurity diffusion in copper of grain boundaries. The effect of internal stresses on boundary diffusion mechanisms, the role of faceting, local thermal disorder, pre-melting and other factors can be reviealed by atomistic methods. Future work in this area is outlined.

Diffusional Properties in Technologically Advanced intermetallics

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We have extensively investigated bulk and grain boundary diffusion in the technologically important Ni- and Ti-aluminides. These compounds exhibit different lattice structures and different types and concentrations of lattice defects on their sublattices (vacancies, anti-structure atoms of constitutional and/or thermal origin) allowing for a restricted number of atomic jump possibilities and diffusion mechanisms. This study therefore provides fundamental insight into the interdependence of diffusion behavior and diffusion mechanisms on structure and ordering.

An overview is presented, including the direct tracer diffusion measurements of the transition metal component and the determination of the Al diffusivity through interdiffusion data and by using Al-substituting solutes, like Ga. The interpretation of the experiments is strongly supported by EAM-potential calculations of defect properties and Monte-Carlo simulations of possible diffusion mechanisms. Among other features, the experimentally established curvature of Ti self-diffusion in TiAl, the surprising effect of the missing diffusion enhancement from structural Ni-vacancies in Al-rich NiAl, and the paradoxically appearing deep minimum of the chemical diffusion coefficient in stoichiometric NiAl are successfully explained.

Some remarks of simultanoeus diffusion of two dopants: diffusion effects and its application in semiconductor devices technology

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The concept of simultaneous diffusion of two dopants has been used and applied in the production of the double diffused semiconductor devices and IC. The simultaneous diffusion method includes, “so call “, the normal sequential and reverse sequential simultaneous diffusion of two opposite types dopants as well as the simultaneous diffusion of two same types dopants.

This paper shows the experiment procedures and diffusion results of the simultaneous diffusion of two dopants (B-As, B-Au, As-P and Sb-P) into silicon. The interaction between dopants and point defect in silicon lattice are shown via several of the abnormal diffusion effects such as Lateral Diffusion Effect (LDE), Retardation Emitter Dip Effect (REDE), Emitter Edge Effect (EEE) and Emitter Dip Effect (EDE). These effects definely reflect the interaction between dopants and point defect The interactions between the dopants or dopant and point defect are explained by so called Kirkendall effect and Coulomb interaction.

The simultaneously diffusion method by reverse sequence has great importance regarding to explain several theoretical problems of diffusion and to use manufacturing several silicon devices. Using simultaneously diffusion method by reverse sequence some kinds of new semiconductor devices may be produced

Diffusion in $L1_0$-type Single Crystal TiAl and FePt Intermetallic Compounds

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Intermetallic compounds have recently attracted much attention for structural materials at high temperatures and functional materials. In particular, γ-TiAl is highly promising light weight and high temperature structural material and FePt is unique magnetic material. The knowledge of diffusion in such compounds is important to understand properties and to fabricate the materials for practical use.

In this talk recent development of diffusion in $L1_0$-type intermetallic compounds of TiAl and FePt single crystals will be presented. The tracer diffusion coefficients ^{44}Ti, ^{59}Fe and ^{103}Pd were measured by an ion-beam sputter-sectioning technique, while the diffusion coefficient of ion-implanted ^{115}In was measured by a secondary ion mass spectroscopy.

In single crystal γ-TiAl of 46at%Ti the anisotropy of the diffusion behavior of Ti is similar to that of In; the diffusion coefficients of both elements perpendicular to the c-axis are three to ten times larger than those parallel to the axis.

In single crystal FePt of 42at%Fe the diffusion coefficient of Fe perpendicular to the c-axis is also larger than that parallel to the axis. The cause of the anisotropy of the diffusion coefficient is discussed in view of the defect structure and the correlation of the jump vectors of successive vacancy jumps.

Furthermore, some impurity diffusion in γ-TiAl and the concentration dependence of the diffusion coefficient of Fe and Pd in FePt will be mentioned.

Application of Scanning Probe Microscopy for Studying of Interfacial Kinetics

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We illustrate how the quantitative information on interfacial thermodynamics and kinetics can be obtained from the *post-mortem* scanning probe microscopy studies of surface topography in the vicinity of grain boundary grooves formed during high-temperature annealing. The examples include the magnetic effect in surface diffusion in pure Fe and Fe-Pb alloys, the measurements of grain boundary energy in Ni-rich NiAl intermetallics, the effect of strong anisotropy in surface energy and diffusivity on the morphology of grain boundary grooves, and the recovery of grain boundary migration kinetics from the topography of new and abandoned grooves.

Diffusion studies in Earth and Planetary Sciences

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Diffusion related processes abound in natural systems and consequently the study of diffusion finds wide applications in the Earth and Planetary sciences. Diffusion in the solid state is often the rate limiting step in many natural processes and therefore measuring rates of diffusion in natural materials amounts to measuring the time scales of geological and cosmochemical processes. Some examples may include the time scale of evolution of volcanic systems, climate change through reactions that take place at ocean bottoms, time scales of mountain building and time scales of condensation in the primordial solar nebula. Thus, the study of diffusive processes provides a bridge between atomic and global or planetary scales. One of the salient recent findings is that contrary to popular intuition, geological processes can occur over time scales relevant to human historical evolution - months, years and centuries are entirely relevant measures of geological time. Study of diffusion in complex natural materials require developments in theoretical and experimental methodology. Treatment of diffusion in complex multicomponent and multiphase systems, often with various simplifying approximations that exploit relationships between variables to reduce the number of parameters to be measured, is a central theme of diffusion related theoretical research in the Earth Sciences. Experimentally, the measurement of diffusion under extremes of pressure, temperature, oxygen fugacity and the measurement of very small diffusion coefficients are the challenges that are met regularly in geosciences. Examples will be discussed.

Some areas where applications are obvious but progress has been minimal include the effects of mechanical stress on diffusion, reactive diffusion and turbulent diffusion.

Diffusion over Long Distances and in Cages: Atoms, Animals, Men and Ideas

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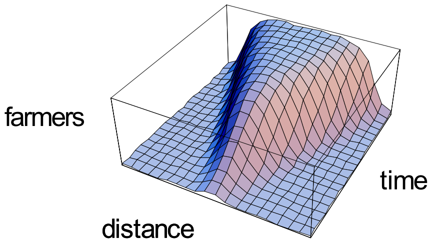
Since several decades diffusion models are invading sciences beyond physics. In favourable cases we can describe the dispersion of plants and animals, of men and ideas in the presence of birth and death, with constructive and destructive interactions.
We shall discuss some of the issues by way of examples from literature:

- The wave of advance of the black death in mediaeval centuries.
- The demic or cultural wave of the agricultural revolution during the neolithicum. The graph shows the dispersion of the neolithic farmers as a function of distance from the origin where farming was invented and as a function of time (all in arbitrary units).



We shall further on present recent results, among them

- The upsetting invasion of the leaf-miner moth causing spectacular aesthetic damage to European horse chestnut trees.

Several of these diffusion phenomena find their correspondence in physics and chemistry, but results from life sciences and cultural sciences are often even more exciting because they pertain to our history, our environment and our human relations.

The Influence of Magnetism on Atomic Defects and Diffusion: Model Calculations and the Ab Initio Electron Theory

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It is well known that the spin polarization which exists in a magnetic material has a pronounced effect on the temperature dependence of the self-diffusion coefficient and the impurity-diffusion coefficient in elementary ferromagnets like Fe and Co or in intermetallic compounds like Fe-Si in the $D0_3$ phase. The first part of the talk reviews the already existing theoretical models for this effect. The major part of the talk explores the effect of magnetism on diffusion in a more fundamental manner by totally switching off magnetism (which can be done in theory). It will be shown by a combination of the ab initio electron theory with statistical mechanics that this induces really dramatic effects in some intermetallic compounds (e.g., B2 Co-Fe and $D0_3$ Fe-Si) which become unstable with respect to the spontaneous formation of atomic defects. This means that magnetism is responsible for the occurrence of the observed phases of these materials in nature as well as for the type of structural and thermal atomic defects and thus for the properties of diffusion.

Random Walk Calculations in Intermetallic Compounds

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It was recognized some fifty years ago that vacancies do not move randomly in intermetallic compounds but, instead, move on complex correlated sequences. But describing these sequences analytically in tracer and chemical diffusion contexts has necessitated considerable theoretical effort. In this paper, we trace the development of models, diffusion mechanisms and random-walk-based i.e. diffusion kinetics calculations in intermetallic compounds. Models to be discussed will include two and four-frequency models and Ising-type models and their variants and adaptations for different structures. Mechanisms to be discussed include the six-jump cycle, the vacancy-pair mechanism, the antistructural bridge mechanism, the triple-defect mechanism, the antistructural sublattice mechanism, the generalized vacancy mechanism and variants of these. Calculations to be discussed include the Path Probability Method, methods inspired by Manning's random alloy diffusion kinetics theory, and calculations based on the five-frequency model adapted to the six-jump-cycle mechanism. It is emphasized how analytical development is especially enhanced when Monte Carlo computer simulation is done in parallel. It is shown, with examples, that a diffusion kinetics theory should be capable of describing both tracer diffusion *and* chemical interdiffusion in a consistent manner. Unsolved problems are highlighted.

Energetics and Efficiency Optimizations of a Simple Brownian Heat Engine

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A simple Brownian heat engine is modeled as a Brownian particle moving in a viscous medium in an external sawtooth potential (with or without load) assisted by the thermal kicks it gets from alternately placed hot and cold heat reservoirs along its path. We get closed form expression for its current in terms of the parameters characterizing the model. After analyzing the way it consumes energy to do useful work, we also get expressions for its efficiency and coefficient of performance when it acts as a refrigerator. Recently suggested optimization criteria enable us to explore and compare the different operating conditions of the engine.

Sedimentation of Substitutional Solute Atoms in Condensed Matter: New Type of Diffusion

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Ultra-strong gravitational field (Mega-gravity field) can realize the sedimentation of even atoms (diffusion), and is expected to create a nonequilibrium crystal-chemical state in multi-component condensed matter. However, the materials science research under mega-gravity field has now remained as an unexploited field, while the sedimentation of molecules or polymer had been used in biochemistory. We presented a self-consistent diffusion equation for sedimentation of atoms in condensed matter. Next, we developed an ultracentrifuge apparatus to generate strong acceleration field of over 1 million ($1x10^6$) g at high temperature up to several 100s degrees C, and, recently, succeeded in realization of the sedimentation of substitutional solute atoms in some alloys of Bi-Sb, In-Pb, Bi-Pb systems, etc. The diffusion coefficients of sedimentation on Bi-Sb alloy etc. were estimated to be much greater than that of normal diffusion due to the internal chemical potential by more than 10, by using a self-consistent theory. In this article, the recent progress in the investigation of sedimentation of atoms under mega-gravity field is shown, and the diffusion mechanism is discussed. The application of the mega-gravity field is also discussed.

HIGH TEMPERATURE DIFFUSION COATINGS BY CVD IN FLUIDIZED BED REACTORS

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The development of protective coatings on materials that operate at high temperatures is an important challenge in the present technology. Al, Si or Si/Al or multilayer is an interesting system from the point of view of protection as to corrosion and for mechanical resistance. The generation of these layers by CVD-FBR (Chemical Vapour Deposition by Fluidized bed) technique is possible with a good yield and low cost, and a temperatures lower than another coating methods, such as pack cementation. This technology represent an interesting alternative to the ferritic steels, since the most of the diffusion coatings can be done at temperature below 600ºC. These protective coatings have been developed for a stainless steel AISI 304 and for some ferritic steels such as P91, P92 and HCM12. These protective coatings were made by Al, Si or Al/Si co-deposition followed of Al deposition or the Si deposition to generate the multilayer system. The obtained results are discussed.

Reactive Diffusion in Nanoscale Systems

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Reactive diffusion is used for metallurgical as well as microelectronic applications. For both applications the tendency is to consider products and reaction zones of more and more limited size. In the next MOS generation, oxides will be in the 1 nm range while reaction and diffusion zones on active parts (source, drain and gate) will be in the 10 nm range. There is thus a need to understand and control reaction at this scale.

Because of microelectronic applications, the literature on reactive diffusion in thin films is extremely well documented. This work (started in the 80's) showed that at the scale of some hundred of nanometers, reaction at interfaces proceed in a different manner than what is observed for bulk diffusion couples: phases appear in a sequential manner, some phases of the equilibrium phase diagram are never observed while metastable products may appear.

More recently the development of *in situ* –real time- techniques (DSC, synchrotron-XRD, …), associated to observation at atomic scale (TEM, atom probe tomography) has allowed to go even deeper in the analysis of reactive diffusion for ultra thin (nanoscale) systems. Developments of non planar fronts, new phases sequences or modifications of the phase sequence with thickness, complex kinetics of formation (multi-stage, non parabolic…) have then been observed. In this presentation we will illustrate these aspects by recent results obtained (by us and others) in nanoscale Al/transition metal or Si/TM couples.

Consequences on Chemical Diffusion and Demixing in Materials of the Sum-Rule Relations Between Phenomenological Coefficients

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In this paper, we first discuss the ‘sum-rule’ relation among the phenomenological coefficients discovered by Moleko and Allnatt for the multi-component random alloy model with the vacancy mechanism operating. The sum-rule gives very considerable simplifications: for example, in the binary system, the number of independent phenomenological coefficients is reduced from three to one. Next we discuss analogous sum-rules recently found by the present authors for a simple model of diffusion by vacancies in an ordered alloy (with random mixing on each sublattice), diffusion via dumb-bell interstitials in the random alloy, diffusion via vacancy-pairs in mixed highly ionic systems. diffusion via divacancies in the random alloy and diffusion via the five-frequency model. Finally, we discuss the consequences of the sum-rule for the analysis of collective diffusion problems in a number of materials, including intrinsic diffusion in binary and ternary alloys, demixing of cations in ternary and quaternary transition metal oxides in oxygen potential gradients and electric fields and intrinsic diffusion and chemical interdiffusion in highly ionic crystals.

Stress Development During the Reactive Film Formation of Silicides

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Thin metal films react with silicon substrates to form various metal silicides. The sequence and kinetics of phase formation are still an area of intense research. Comparatively much less work has been done on the issue of stress development caused by the appearance of these new phases. A detailed review of the subject has been done ten years ago. We want here to present new results obtained during these recent years on Pd-Si, Co-Si, Ni-Si and discuss them in the light of what is known today on the elastic and plastic properties of thin films.

A simple model published by S. L. Zhang and F. d'Heurle takes into account the simultaneous stress formation due to the reaction and the relaxation of these stresses. It provides a qualitatively satisfying picture of stress evolution at least for the first phase which forms. The model relies on two basic elements: 1) stress formation due to the formation of a new phase, and 2) the stress relaxation mechanism at work in the growing silicide film. The sign of the stress can be understood from the variation in volume that occurs at the growing interface(s). The role of epitaxial strains still remains to be understood (in the case of Pd_2Si on Si (111), the stress was shown to be compressive, as predicted from volume considerations, whereas epitaxial strain should have produced a tensile stress). The stress relaxation mechanisms at work in a growing film are complex. They are highly dependent on the microstructure (as we have shown when comparing Pd/Si(001) and Pd/Si (111)) but should be also highly size dependent (e.g. dislocation glide is more difficult in small scale structures). In addition the relaxation mechanisms at work are highly dependent on the temperature range (dislocation glide or climb, creep, …).

Computer Simulation of Phase Decomposition in Magnetic Materials Based on the Phase-field Method

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During the last decade, the phase-field method has emerged across many fields in materials science as a powerful tool to simulate and predict complex microstructure evolution, (e.g., dendrite growth, spinodal decomposition, Ostwald ripening, crystal growth, recrystallization, martensitic transformation, dislocation dynamics, electromigration, crack propagation, and so on). Since phase-field methodology can model complex microstructure changes quantitatively, it is possible to search for the most desirable microstructure by using this method as a design simulation, i.e., through computer trial-and-error testing. In order to carry out this methodology, the flexible quantitative modeling method for complex microstructure changes using the phase-field method must first be established.

In this study, as the typical examples for the modeling of the complex microstructure changes using phase-field method, I will demonstrate the recent simulation results for the diffusion controlled phase transformations and microstructure developments in magnetic materials, for example, 1) the spinodal decomposition in Fe-Cr-Co hard magnetic alloys under external magnetic field, 2) Cu-cluster formation in amorphous Fe-Si-Cu alloy during isothermal aging, 3) FePt nano-granular structure formation during sputtering and the order-disorder phase transition of FePt nano particles, 4) Twin macrostructure developments in Ni_2MnGa ferromagnetic alloy under external stress and magnetic field, 5) the phase transformation and microstructure changes in Co-Sm-Cu hard magnetic materials, etc. Furthermore, I will discuss the relation between the calculated microstructure morphology and the magnetic hysteresis loop through the micromagnetics calculation.

Interfacial Reactions in the Cu-Ni/Sn System

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In recent years, ternary alloys based on Sn-rich, Sn-Cu and Sn-Ag binary eutectics, have attracted considerable attention as potential Pb-free solders. However, intermetallic layers formed at the interface between the solder and pads of a printed circuit board may adversely affect the reliability of solder joints due to excessive growth during storage and service.

Solid state reactions between lead free solders and Cu or Cu-Ni substrates are studied at temperatures ranging from 150 to 210°C. Two binary intermetallic layers, Cu_6Sn_5 (η-phase) and Cu_3Sn (ε-phase) are formed at the interface between the solder and Cu substrate. The presence of Ni in the system - expected to decrease the interfacial reaction rate, leads in the contrary to a major increase of the growth kinetics of the brittle η-phase. Thermodynamic and/or kinetic reasons of this surprising result are discussed.

Synthesis and Stability of Silicide/semiconductor Interfaces for Microelectronics Application: Diffusion and Reaction

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The use of metallic silicide is primordial to obtain integrated circuits with very high devices density and speed. Indeed silicide allow to reduce the contact and interfacial resistance of the active parts of transistors and memories. Another crucial advantage of the silicides is that they can be incorporated in devices by the salicide process (self aligned silicidation). This process based on the solid state reaction between a metal film and silicon allows to increase the integration level by selective formation of the silicide on the active parts of the silicide.

The synthesis and stability of silicide/silicon interfaces are primordial. In this presentation, some example concerning the synthesis and stability of the silicide used in microelectronics ($TiSi_2$, $CoSi_2$ et NiSi) will be presented. Some elements of understanding of the involved phenomena will be developed using a thermo-kinetic approach.

The use of $TiSi_2$ and $CoSi_2$ is meeting metallurgical limitations for linewidth below 0.15 µm. To illustrate these limitations, we will present the effect of dimensions on the formation of C49-$TiSi_2$.

It has been shown that NiSi can be used for transistors with dimensions below 0.1 µm. Yet two problems are still present: i) around 600-700°C, the NiSi film become discontinue and agglomeration occurs, ii) around 700-800°C, NiSi is transformed in $NiSi_2$. We have shown that the addition of a small quantity of platinum limits the agglomeration and stabilizes the NiSi/Si interface by delaying the formation of $NiSi_2$. With the continuous decrease of features size in microelectronics, it is also necessary to decrease the film thickness and the first stages of silicide formation are important. We will present some results concerning the first stages of formation of nickel silicides.

Diffusion of Lithium in Surface Modified Electrode

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Surface modification of natural graphite anode by thin layer of oxide improve the rate property of lithium ion battery[1]. In this paper, we will present the rate property and the diffusion mechanism by the surface modification of $LiMn_2O_4$ cathode by aluminum oxide nano-layer.

The surface modification of $LiMn_2O_4$ particles was carried out by a kind of sol-gel method. One gram of $LiMn_2O_4$ was put in 100 ml of 2-propanol containing 10 mmol/dm^3 of Al-isopropoxide. This mixture was stirred under ultrasonic treatment and then filtered. The precursor obtained was heated at 400 degree C. Thus $LiMn_2O_4$ particles with partly surface modified by alumina (around 20 nm) was prepared. From the Al-K-edge XANES spectra, alumina was amorphous. The surface modified $LiMn_2O_4$ showed better charge-discharge property with high rate compared with pristine $LiMn_2O_4$. The diffusion coefficient of lithium was evaluated from the results of AC impedance. As shown in Fig 1, the diffusion coefficient for both pristine and surface modified samples was same. It seems that the electrode surface play an important roll for charge transfer. Actually, the charge transfer resistance of surface modified sample was smaller than that of pristine sample. Even in oxide cathode, the thin layer of SEI will form on the surface of $LiMn_2O_4$. We assume that the lithium on the surface of the surface modified oxide diffuses more easily than in the SEI. Alumina in the grain boundary may contribute easier diffusion of lithium than SEI as shown in Fig. 2.

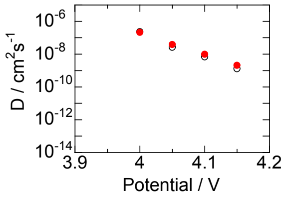

Fig.1 Chemical diffusion coefficients of lithium in Al-modified and unmodified $LiMn_2O_4$.

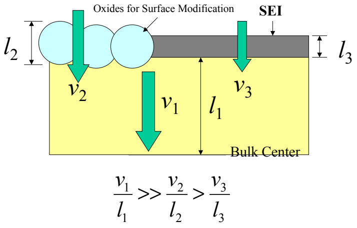

Fig.2 Diffusion model of surface modified sample.

[1] S-S Kim, Y. Kadoma, H. Ikuta, Y. Uchimoto and M. Wakihara, *Electrochem. Solid-State lett.*, 4, A109 (2001).

Non-linear Effects in Diffusion on Nanoscale

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Diffusion on very short distances in amorphous materials, epitaxial multilayers, during dissolution of thin films or kinetics of surface segregation has many challenging features even if the role of structural defects (dislocations, phase- or grain-boundaries) can be neglected and “only” principal difficulties, related to nanoscale effects, raise. Different examples for diffusion in such materials will be given with special emphasis on the validity limit of the continuum approach especially if the diffusion coefficient depends strongly on composition (non-linearity). Even in ideal systems (like Cu/Ni) this non-linearity leads to *linear* shift of an originally sharp interface (instead of the parabolic behaviour) and to sharpening of an initially diffuse interface. The sharpening takes place, even if the effects of stresses (built in mismatch, thermal and diffusional stresses) are taken into account. Deviations from the parabolic law are present in phase separating systems as well, but here the interplay of the strong composition dependence and the phase separation tendency results in a more complex behaviour. These deviations are typical nanoeffects i.e. they diminish after dissolution of several hundred atomic planes.

Redistribution of doping elements in SiGe nanostructures

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Even if the production of new devices based on SiGe compounds has dramatically increased these last years it remains centred on HBT devices with low Ge concentration. This is because of some fundamental growth problems that have to be solved before reliable production of new SiGe devices such as MODFET. One of the major problems is for instance, the fabrication of high concentration SiGe layers highly doped, with sharp interfaces. The aim of this study is to determine the growth conditions that permit to reduce the two major mechanisms of dopants redistribution i.e. dynamic segregation during growth and diffusion during oxidation.

In this study we analyse the redistribution of two doping elements (Sb for type N and B for type P) as a function of epitaxial stress (compressive and tensile) and Ge composition independently. Diffusion coefficients (D_{Sb}) have been determined by simulation of the SIMS profiles before and after UHV annealing. Segregation coefficients are deduced from the incorporation coefficient obtained by analysis of the SIMS profile of as grown samples. We show that diffusion coefficient of Sb increases with x in relaxed layers and in epitaxial compressively strained layers but decreases in epitaxial tensily strained layers. Opposite behaviour is obtained for B diffusion mechanism. In parallel, the investigation of segregation shows that segregation of Sb increases with the growth temperature and with the Ge composition in epitaxial compressively strained layers and decreases with x in relaxed layers. Again opposite results were obtained for B segregation. Diffusion and segregation of the two elements are explained and discussed. We show the good agreement between our results and the vacancy and interstitial mediated diffusion of Sb and B respectively.

Grain Boundary Phase Transitions. Influence on Diffusion and Transport Processes

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Grain boundary (GB) phase transitions change drastically the GB diffusion and transport properties. The GB wetting phase transition can occur in the two-phase area of the bulk phase diagram where the liquid (L) and solid (S) phases are in equlibrium. Above the temperature of the GB wetting phase transition a GB cannot exist in equlibrium contact with the liquid phase. The experimental data on GB wetting phase transitions in the systems Al–Sn, Al–Ga, Al–Sn–Ga, Cu–In, Cu–Bi, Fe–Si–Zn, Mo–Ni, W–Ni, Zn–Sn and Zn–In are analysed. The GB wetting tie-line can continue in the one-phase area of the bulk phase diagram as a GB solidus line. This line represents the GB premelting or prewetting phase transitions. The GB properties change drastically when GB solidus line is crossed by a change in the temperature or concentration. Between GB and bulk solidus the thin layer of GB phase appear which is unstable in the bulk and stable in the boundary. The experimental data on GB segregation, energy, mobility and diffusivity obtained in various systems like Cu–Bi, Al–Ga, Al–Pb and Fe–Si–Zn both in polycrystals and bicrystals are analysed. In case if two solid phases are in equilibrium, the GB “solid phase wetting” can occur. In this case the layer of the solid phase *2* has to substitute GBs in solid phase *1*. Such GB phase transition occurs if the energy of two interphase boundaries is lower than the GB energy in the phase *1*. The experimental data on GB “solid phase wetting” in systems Zn–Al, Cu–In, W–Ni, W–Cu and Mo–Ni are analyzed.

Solute Segregation Studied by Grain Boundary Diffusion

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Radiotracer grain boundary (GB) diffusion measurements have established themselves as an impressive and powerful tool for studying GB segregation. The key point here is the combination of GB diffusion experiments in so-called B and C kinetic regimes, in which the triple product $P = s\delta D_{gb}$ and the GB diffusivity D_{gb} respectively are accessible. Here s is the segregation coefficient and δ the GB width. Using the value of the GB width $\delta \approx 0.5$ nm established from GB self-diffusion measurements, the segregation factor s is determined as: $s = P/\delta \cdot D_{gb}$. Applying a solute-radioisotope with a well-defined specific activity the absolute amount of the solute in a GB can be estimated as a function of the penetration depth. Typical radiotracer experiments on a polycrystalline material were shown to correspond to the truly dilute limit of solute segregation. This approach has successfully been applied for several solutes in Ag and Cu matrixes and the systematics of GB diffusion and segregation in these systems is reported.

The amount of solute atoms in a GB can be increased by performing diffusion experiments on bicrystals and alloyed polycrystals. This allows us the quantitative study of non-linear solute segregation. In suitable cases, even a segregation isotherm can be derived, as it is demonstrated e.g. for Ag GB segregation in Cu.

GB diffusion experiments in the C kinetic are really laborious by the requirements to detect tiny amounts of solute atoms in the limited number of GBs of a well-annealed polycrystalline material. However, the counting statistic can decisively be improved by applying the same material with a nanocrystalline grain size e.g. when investigating oversized solute atoms with a very low solubility in the GBs. Combining GB diffusion experiments in coarse-grained and nanocrystalline alloys the Ag GB segregation was investigated in the Fe-40 wt.% Ni alloy. Since the nano-material under consideration revealed a two-scale microstructure (the nano-grains are clustered in micrometer-large agglomerates), a new diffusion problem arises which will be discussed in detail.

Kinetic Methods in Studying the Transport Properties of Transition Metal Oxides and Sulphides

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Due to the variable valence of cations, transition metal oxides and sulphides show deviation from stoichiometry, resulting from the disorder prevailing in one sublattice only. Thus, transport properties of these compounds may be explained in studying the kinetics of nonstoichiometry changes as a function of temperature and oxidant activity using modern microthermogravimetric techniques. It has been shown that chemical diffusion coefficient and thereby the mobility of predominant defects in these compounds can be successfully studied using re-equilibration and two-stage kinetic methods, however, at oxidant pressures much higher from the dissociation pressure of a given oxide or sulphide. The third kinetic method eliminates this limitation by creating the possibility to calculate the self-diffusion coefficient of cations from evaporation rate of metal atoms into vacuum from the surface of the oxide or sulphide scale being in the equilibrium with the metallic phase, i.e. at lowest oxidant activity. These methods are shortly discussed and their adventages are illustrated by the results obtained on $Mn-Mn_{1\pm y}S-S_2$ system, which has been extensively studied by different authors using various experimental techniques.

Unified Simulation of Diffusion in Silicon and Silicon Dioxide

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The simulation of diffusion in silicon and silicon dioxide becomes more important with the scaling down of Si device size. The simulation should be done in a unified manner so that it is applicable to wide ranges of process conditions, and therefore, should be based on the diffusing dopant species and point defects that primarily contribute to dopant diffusion. Intrinsic point defects and diffusion mechanisms in Si have been studied in these decades. Based on the knowledge, we have integrated a basic diffusion model (1). We will first present the simulation of P diffusion in Si based on the model and elucidate the mechanism of the appearance of the anomalous P in-diffusion profile. The vacancy mechanism governs the diffusion in the plateau region, while the kick-out mechanism governs it in the deeper region, where Si self-interstitials dominate in the kink region and P interstitials dominate in the tail region (1).

In the second part, we will present our recent results on Si self-diffusion (SD) in SiO_2. We examined the diffusion of implanted ^{30}Si in thermally grown $^{28}SiO_2$, which showed increasing self-diffusivity with decreasing distance between the ^{30}Si diffusers and Si/SiO_2 interface (2). We propose a model in which SiO molecules generated at the interface and diffusing into SiO_2 enhance the SD. The simulation showed that the SiO diffusion is so slow that the ^{28}SiO concentration at the ^{30}Si region critically depends on the distance from the interface. Moreover, the simulation predicts the possibility of time-dependent SD because more SiO molecules should be arriving from the interface with time. As predicted, the time-dependent diffusivity was experimentally observed, and this confirms our model.

The research on diffusion in oxide was collaborated with H. Kageshima, Y. Takahashi (NTT), S. Fukatsu, K. M. Itoh (Keio Univ.), K. Shiraishi (Univ. of Tsukuba), and U. Gösele (MPI, Halle).

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Thermal Defects and Diffusion in $MoSi_2$

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The intermetallic compound $MoSi_2$ with a $C11_b$ structure is considered as a potential high-temperature material because of its high melting temperature and its low mass density. Positron lifetime studies show that no structural vacancies are present in $MoSi_2$ and the formation of thermal vacancies has been detected with a relatively low vacancy formation enthalpy of H_V^F=(1.6±0.1) eV and an estimate of a low migration enthalpy H_V^M [1]. Results of coincident measurements of the Doppler broadening of the positron-electron annihilation line at high electron momenta in combination with data for positron annihilation in $MoSi_2$ derived from theory demonstrate that thermal vacancies in $MoSi_2$ are preferentially formed on the Si-sublattice [1]. The present studies of high-temperature vacancy formation can be directly employed for an immediate understanding of recent self-diffusion studies of ^{31}Si [2] and of ^{99}Mo [3] in $MoSi_2$.

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Influence of Interfaces on the Morphological Evolution of Electric Field Driven Solid State Reactions

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Along with ongoing miniaturisation of ceramic devices the volume fraction of internal surfaces is increasing. Solid state reactions, negligible on macroscopic length scales, become more important in the nanoscale. During operation ceramic materials are often exposed to high electrical fields, which create a second driving force for mobile components in addition to the chemical potential gradient. Currently, only a small number of studies on solid state reactions in external electrical fields can be found [1], [2]. The aim of this study is to investigate the influence of an external electric field on the morphological evolution, the kinetics and the microscopic mechanism of a solid state model reaction. Using linear transport theory, a time independent and strongly enhanced growth rate for a spinel product layer can be predicted, when the trivalent oxide is attached to the cathode side in an electrochemical cell. The role of grain boundaries as fast diffusion paths is also highly emphasized. Thus, the morphology of the product layer is significantly different compared to a non field-driven reaction.

The electrochemical cells for our experiments were made in thin film technique by means of PLD. The morphological evolution of the boundaries, the microscopic structure and the crystallographic orientation of the adjoining phases are investigated by FESEM (EDX) and TEM.

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Self- and Interdiffusion in Ternary Cu–Fe–Ni Alloys

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Lattice diffusion of ^{64}Cu, ^{59}Fe, and ^{63}Ni radiotracers has been measured in Cu–Fe–Ni alloys of different compositions at 1271 K. It has been found that most of the measured penetration profiles (especially for Fe diffusion) show both extended grain boundary-induced part and the initial bulk diffusion induced one. Grain boundary diffusion contribution was consistently taken into account when determining the bulk diffusivities of the components. When the Cu content in the alloys increases, the diffusivities increase by order of magnitude. This behaviour correlates well with decreasing of the melting temperature of corresponding alloys, as the Cu content increases.

Modelling of interdiffusion in the Cu–Fe–Ni system based on Darken's method of interdiffusion for multi-component systems is presented. A postulate that the total mass flow is a sum of the diffusion and the drift flows, was applied for the description of interdiffusion in the bounded system. Nernst-Planck's flux formula assuming a chemical potential gradient as a driving force for the mass transport was used for computation of the diffusion flux in non-ideal multi-component systems.

In computations of the diffusion profiles the measured tracer diffusion coefficients (Cu, Fe, Ni) and the literature data on thermodynamic activities for the Cu–Fe–Ni system were used. The calculated interdiffusion concentration profiles (diffusion paths) are compared with the experimental results.

Atomic Transport Measured by Analytical Electron Microscopy Technique

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Most of the changes in the structure occur by thermally activated mass and charge transport through the matter, called diffusion. The most important information concerning the rate controlling factor can be determined from the solute partitioning, which accompanies the changes in the microstructure. In many cases, the solute redistribution occurs within a narrow area of nanometer order. Such highly localised changes in chemistry can be detected using an analytical electron microscopy (AEM). The present paper reviews the capabilities of AEM showing the following examples:

- diffusion couples and precipitation of grain boundary allotriomorphs (determination of intediffusion coefficient),
- discontinuous precipitation (determination of grain boundary diffusivity),
- austenite to intragranular ferrite and bainitic transformation (determination of transformation mechanism).

Flux-Driven Coarsening in Open Systems

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Some new results on ripening and grain growth in open systems will be briefly reviewed:

Flux-driven ripening (FDR) of scallops of Cu6Sn5 or Ni3Sn4 during reaction between copper or nickel with tin-based liquid solder is analyzed. In this process the new-formed intermetallic compound (IMC) is growing in the form of scallops separated by narrow liquid channels with bottom at the very substrate. The total area of scallop/melt interface appears to remain approximately constant and total IMC volume grows as $t^{1/3}$. It is quite different from usual ripening (decreasing area and almost constant volume). New kinetic theory of FDR is presented. Growth and ripening rate appears to be independent (explicitly) on surface tension but proportional to channel with and diffusivity of Cu/Ni in melt.

Flux-driven grain growth (FDGG) occurs in thin films during deposition. Under deposition of polycrystalline thin film of many fcc metals the average lateral grain size is nearly the same as the film thickness. It means that the very process of deposition helps larger grains to grow (in lateral directions) at the extent of smaller grains. So, if the rate of the atom deposition is constant the lateral grain growth rate is linear. We propose simple analytical and Monte Carlo models of this process. Idea of FDGG is modified to describe the lateral grain growth in newly formed layer of IMC during reactive diffusion (reaction-driven grain growth - RDGG).

New approach to the normal grain growth and to diffusive coarsening (ripening) is presented. Main idea is the formulation of thermodynamics and kinetics of self-similar stage of coarsening in the normalized (scaled) space. Such approach enables us to obtain the size distributions much more close to experimental data than the standard LSW and Hillert approaches.

Dynamics of Superstructure Formation in Intermetallic Compounds

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High superstructure stability in a number of technologically attractive intermetallic compounds causes that the state of chemical long-range order (LRO) is often maintained up to the melting point. Fine temperature dependence of the degree of long-range order is, however, experimentally observable in such systems in so-called "order-order" relaxation processes. Due to the high degree of LRO the phenomena are controlled by atomic migration in almost perfect superstructure. They proceed, however, in *non-steady-state* of a system, which relaxes to the equilibrium atomic configuration. Hence, the investigation of "order-order" kinetics is complementary to standard *steady-state* diffusion studies.

Extensive experimental research of Ni_3Al ($L1_2$), NiAl (B2), FePd ($L1_0$) and FePt ($L1_0$) showed two time scales operating in the relaxations observed in Ni_3Al and FePd. Surprisingly slow relaxations were observed in NiAl – known of a giant vacancy concentration. Definite relationships between the activation energies for diffusion E_A^D and "order-order" relaxations E_A^O were revealed: $E_A^D < E_A^O$ in $L1_2$; $E_A^D > E_A^O$ in $L1_0$ and $E_A^D > E_A^O$ in B2.

Corresponding simulation studies elucidated the specific atomistic mechanism of the processes. It has been shown that different time scales active in experimentally monitored "order-order" relaxations in $L1_2$ and $L1_0$-ordered systems follow from specific atomic-jump correlations, which result from non-steady-state conditions and particular superlattice geometries. A model of "order-order" kinetics in NiAl as controlled by a triple-defect mechanism is proposed. The process is, however, not tractable by means of MC simulation with currently available computer codes.

Anomalous Behaviour in Hydrogen Diffusion through Palladium and Metal-Hydrides

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Hydrogen transport through Pd and metal-hydrides has been usually investigated by using potentiostatic current transient technique (chronoamperometry), on the basis of the diffusion-controlled model. This assumes that hydrogen diffusion in the electrode is very slow, while other reactions including interfacial charge transfer and hydrogen transfer are too fast to influence hydrogen transport, and thus hydrogen transport is purely governed by hydrogen diffusion. However, various kinds of anomalous behaviour in hydrogen transport, which could be hardly explained by the diffusion-controlled model, have been quite frequently reported by many researchers.

In particular, we propose that the diffusion-controlled model should be no longer valid in case hydrogen transport through such hydride-forming electrodes as Pd and metal-hydrides proceeds under the constraint that hydrogen diffusion is coupled with either interfacial charge transfer or hydrogen transfer reaction or with both reactions. The anomalous hydrogen transport models suggested are theoretically described with the mathematical expressions for the current transient, and then they are exemplified by hydrogen extraction from the Pd and metal-hydrides in aqueous solutions. Finally, some parameters affecting hydrogen transport, e.g. the potential step and the nature of the electrode surface, are discussed in detail.

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Liquid Metal Embrittlement : Fast Diffusion Under Stress / Strain Gradients

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When wetted by certain liquid metals (LM) and under tensile stress, many solid metals show fast failure. The most harmful degradation mode is accelerated growth of subcritical cracks which cavities are filled with LM. Our SEM micro-crack kinetic study performed for the model system 5N polycrystalline Cu $_{S0LID}$ – $[Bi_X\ Pb_{1-X}]_{LIQUID}$ has shown the following:
(i)Crack growth is thermally activated process with low $E_{act} \approx (0.3\text{-}0.4)$ eV
(ii)Crack extension rate V grows exponentially as the specific surface energy $\gamma_{SL}(x)$ at the Cu/liquid interface decreases with x.
(iii)Equilibrium GB segregation of all the alloying elements studied (including Sb and Bi which are known to cause severe GB embrittlement of Cu in inert atmosphere) reduces V and its γ_{SL} dependence.
(iv)Existence of the threshold stress –intensity factor K_{TH} ; at $K > K_{TH}$ the crack velocity V increases steeply and can reach $V \neq f(K)$. $\sim 10^{-1}$ m /s .
We proposed that wetting does not introduce new failure mechanisms, but simply *accelerates* well known *diffusion controlled* mechanisms of crack extension. The main accelerating factors are considered to be i) *fast diffusion of metals in liquid phase* that enables fast mass transfer out of the crack tip and ii) *wetting induced surface reconstruction* , transition to atomically rough surface , in particular at low γ_{SL} ; this enables fast detachment / attachment reactions at the liquid -solid interface.
We discuss then two versions of the proposed mechanism of LME. In the first of them (" Robertson –Glickman model") the remote tensile *stress* σ increases chemical potential at the crack tip $\mu \propto K^2 \propto \sigma^2$ that is creates the thermodynamic driving force for crack extension by the dissolution – diffusion – deposition process [2] . In the second one, GB crack extends by *spontaneous* process of the Mullins grooving, which is dramatically accelerated by blunting the tip due to local plastic *strain* [2].

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Ageing of Oxides in Irradiation Environment

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The complex nature of bonding in oxides, partly ionic and partly covalent, has been for long a difficulty for defects and ageing studies, particularly in irradiation environment. In this talk we will present the main steps of a modelling of this ageing, from primary defect creation to collective behaviour, putting the greatest emphasis on the recent progresses allowed by the present day modelization capability, whether based on empirical or quantum ab-initio Hamiltonian. We shall then review defect creation threshold studies, microstructural evolution during irradiation, radiation induced diffusion, and phase changes.

Interdiffusion between Metals of Widely Different Self-diffusion Rates

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Investigation of interdiffusion between alloys of widely different characteristic is interesting in view of the fact that several anomalous features appear during interdiffusion owing to the large difference between the flux of diffusing species. In some binary systems, it has been observed that the interdiffusion coefficients determined by multi-phase couples are smaller than those determined through single phase couples. This observation implies that the Boltzmann-Matano analysis is unapplicable to such cases. In the present article, this phenomenon is reviewed. Recent experimental results on interdiffusion enhanced under elevated hydrogen pressures are also discussed.

The Kirkendall Effect in Solid State Diffusion

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Recently, the presence of two Kirkendall planes has been discovered in solid-state diffusion couples in various binary metallic systems in our laboratory, and in this work even three Kirkendall marker planes were found in a couple Ti/TiAl$_3$. The bifurcation and trifurcation of the Kirkendall plane can quantitatively be described using the classical diffusion theory in terms of Kirkendall velocity construction. The position of a Kirkendall plane is revealed in the reaction zone not only by inert markers, but also by a different crystal morphology on either side of the plane.

A physico-chemical approach is developed which elucidates the role of the Kirkendall effect in the morphogenesis of interdiffusion systems. The occurrence of one or more Kirkendall planes, characterized by morphology changes in the reaction layers, turns out to be related to different nucleation sites of the product grains. The model is demonstrated using the experimental results in the Co-Si system. It is shown that the predictions using the physico-chemical approach are in good agreement with the experimentally found positions of the Kirkendall plane(s). The presence or absence of inert markers at the Kirkendall planes provides insight into the initial stages of reactive phase formation.

Modelling, Simulations and Monitoring of Lamella Structure Formation in Titanium Alloys Controlled by Diffusion Redistribution

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A mathematical model and computer programs are developed for simulation and monitoring of the processes of nucleation and growth of the α phase Widmanstätten plates during the course of the $\beta \Rightarrow \alpha$ phase transformation in titanium alloys. Based on integration of thermodynamic modelling and finite element simulations, the α phase appearance at the grain boundary of β phase is described by a numerical procedure for random nucleation as a function of the alloy composition and the temperature. The rate at which an interface moves depends both on the intrinsic mobility and on the rate at which diffusion can remove the excess of β stabilising atoms ahead of the interface. This process is controlled by diffusion redistribution of the alloying elements between the α and β phases that are different for different titanium alloys. The finite element method was used for solving the diffusion equation on the domain occupied by β phase. The models and program packages developed are used to simulate the morphology of the microstructure evolution (Fig. 1) in different titanium alloys during variety of heat treatment processings and can be used in the real processing route.

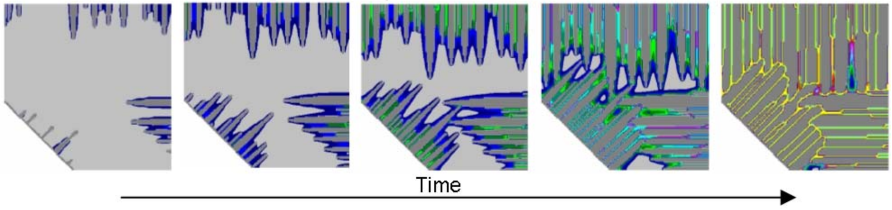

Fig.1 Simulations for the microstructure evolution of the $\beta \Rightarrow \alpha$ phase transformation in Ti-6Al-2Sn-4Zr-2Mo alloy at continuous cooling.

Diffusional Jumps of Intrinsic Atomic Defects in Ordered Alloys Observed through Anelastic Relaxation Effects

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In ordered structures it may happen that the positions of some of the constituent species are of lower symmetry than that of the host crystal. In such cases any atomic defect, e.g. vacancies, wrong-site atoms or impurities, forms a low-symmetry defect, which can undergo stress-induced reorientation, i.e. redistribution, among crystallographically equivalent but directionally distinct sites under external stress. The anelastic relaxation effect caused by the redistribution allows us to access to the concentration of the defect and its mobility. We will report such relaxation effects observed for some ordered alloys of the $L1_2$ structure, which is believed to be caused by the reorientation jumps of antistructure atoms of the minority species [1].

The phenomenon is similar to the case of interstitial solutes in b.c.c. metals (the Snoek effect), for which relaxation experiments have successfully been applied to determination of the diffusion coefficients. Generally, however, converting the atomic jump frequencies obtained from the relaxation rates to diffusion coefficients is not a straightforward task. It is nevertheless possible, provided that the mechanism of the long-range diffusion is known and quantitative information on the parameters involved in the diffusion process are available. As an example, we will show the diffusion coefficient of Al in Ni_3Al evaluated from such an analysis.

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Oxygen Diffusion in Alumina. Application to Synthetic and Thermally Grown Al_2O_3

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^{18}O diffusion coefficients have been determined in Al_2O_3 scales thermally grown on various Fe-20Cr-5Al steels with or without RE additions. The oxygen isotope profiles collected by SIMS allowed to determine bulk and grain boundary ^{18}O diffusion coefficients. Previous two-stage oxidation experiments have been performed to determine the Al_2O_3 scale growth mechanism. It clearly appeared that a mixed anionic-cationic diffusion mechanism is responsible for the alumina scale growth on undoped FeCrAl and Zr-doped alloys. For the other doped specimen, oxygen diffusion was found to be predominant. The diffusion experiments were compared to kinetic tests performed under air in a thermobalance.

The role played by the reactive elements (Y, Zr, Hf, La , Ce,…) on the oxygen diffusivity will be discussed.

^{18}O diffusion coefficients were also determined in synthetic alumina. Y-doped alumina powders were prepared via an humid route from a slurry of high purity α-Al_2O_3 powder and a nitrate solution. Samples were then CIPed and HIPed to get very dense translucent polycrystalline samples. The so-calculated ^{18}O diffusion coefficients were compared to the coefficients determined on thermally grown alumina scales and to the data issued from the literature.

The final discussion will be focused on the possibility or not to compare accurately synthetic and thermally grown alumina to determine oxygen diffusion coefficients.

Charge Transport Processes in Biomaterials: Electron Transfer in Proteins and Gating Kinetics of Biological Channels

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Continous time and space Markovian random processes are capable of modeling various types of biological transport processes such as charge transfer in complex media, ligand migration in proteins or gating kinetics of biological ion channels. The formalism of stochastic diffusion easily incorporates effects of fluctuating environments and is a legitimate method to study positive influence of noises on overall dynamics of mesoscopic systems. I will report on several aspects of biological efficiency in tuning to noise with an emphasis on phenomena of resonant activation, stochastic resonance and hysteresis.

Scaling Poperties of the Diffusion Process Underlying the Havriliak-Negami Relaxation Response

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Continuous-time random walk (CTRW), introduced by Montroll and Weiss more than 40 years ago, have proven to be a versatile matematical tool for description of many anomalous kinetic phenomena. The application of this techniques to photoconductivity of disordered semiconductors by Scher and Montroll was a milestone in understanding of dynamical properties of disordered systems.

The notion of CTRW generalizes a simple random walk by implementing a random waiting time between jumps. This stochastic process is defined by the total distance $R(\tau)$ reached by a walker if the movement is generated by a sequence $\{(R_i,T_i)\ i = 1,2,...\}$ of jump parameters. R_i denotes both the length and the direction of the i-th jump, while the positive variate T_i is the waiting time for the i-th jump.

The intimate connection between the CTRW with heavy-tailed waiting-time distributions and stable laws was clear from the very beginning and was stressed in the approach based on the concept of fractal time, advocated by Shlesinger. The practical use of this connection, however, was rather sporadic. Therefore, we find it reasonable to reestablish some old and more recent results in the field, using the approach that stress that deep connection, namely the one based on limit theorems of probability theory. Since this approach uses a language which is unfamiliar to most in the physics community, we give a concise introduction into random variables and limit theorems before we approach the question of limit distributions of the CTRW underlying the Havriliak-Negami relaxation response. The concept of limit distributions in a natural way can be expressed as a scaling property of a coarse-grained long-time asymptotic behavior.

Spectroscopic Studies of Diffusion and Reaction in Complex Oxides

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Spectroscopic studies can provide insight into a large variety of physical and chemical processes in solids. In this contribution, we report on spectroscopic investigations into the diffusion and the redox behaviour of complex oxides, like olivines and garnets. Diffusion and reactivity in these solids is studied by means of Mössbauer spectroscopy and by optical spectroscopy. Results reported have been obtained by *in situ* experiments performed at high temperatures and at defined conditions of oxygen partial pressure.

Atomic migration of Fe^{2+} ions in the iron silicate Fe_2SiO_4 (fayalite) has been studied by analysing the diffusion-broadened high-temperature Mössbauer spectra of the material. Diffusion of iron can be detected and distinguished on the two sublattices M1 and M2 of the olivine structure. Diffusion on the M1 sublattice is found to be faster than that on M2 sites. From the dependence of atomic jump frequencies on oxygen partial pressure it is concluded that iron ions migrate by means of a vacancy mechanism. Results are corroborated by a high-temperature optical spectroscopy study into the kinetics of redox processes in single crystalline Fe_2SiO_4. The orientation dependent study shows that the diffusion of cation vacancies is fastest in the c-direction of the orthorhombic olivine structure. Analogous optical studies of reaction kinetics have also been performed on isostructural Co_2SiO_4.

The formation of Yb^{2+} ions in the $Yb_3Al_5O_{12}$ garnet is studied by means of optical spectroscopy at temperatures between 800°C and 1200°C. The reduction and re-oxidation of the material has been found to follow the two different reaction mechanisms of external reduction and internal oxidation. Transport and reaction kinetics are discussed in the framework of diffusion of electrons, holes, and anion vacancies.

Reactive Diffusion in the Ni-Si System: Phase Sequence, Texture and Agglomeration in Thin Films

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Interest in low resistivity NiSi has increased significantly because of its current use in advanced microelectronic devices. This scrutiny has lead to new insights, first vis-à-vis the phase formation sequence at low temperature and then regarding the texture of the low resistivity NiSi phase and its tendency for early agglomeration. Despite the similar behavior of Ni/Si and Co/Si films in traditional studies, it has become clear that the phase sequence for Ni/Si films is more complex, as studied using *in situ* measurements. Isothermal and ramp anneals of Ni films (10 to 500 nm) demonstrate the presence of multiple metal-rich phases, some of which showing a formation possibly controlled by nucleation.

Recent extensive measurements of texture in NiSi films on single crystal Si substrates [1] showed a very strong axiotaxy texture in which planes with "equal" spacing in the substrate and film tend to align. This alignment corresponds to a low energy interface that is periodic along one direction within the interface. Interestingly, since the periodicity originates from plane alignment, the lower energy interface does not depend on interfacial roughness. As a result, when NiSi starts to form, the inherent roughness of these early stages should favor the formation of grains with planes that are aligned with planes of the surrounding substrate. For the very thin NiSi films, upon heating, the layer suffers from morphological degradation before it transforms to the thicker $NiSi_2$ phase. Surprisingly, the agglomeration of NiSi films is considerably faster for films formed on crystalline Si compared to poly-Si substrates. The large anisotropy in thermal expansion for the NiSi and the strong texturing of the NiSi film on crystalline silicon substrates represent two important factors in this observed behavior.

1- C. Detavernier et al, Nature **426**, 641 (2003).

Chemical Diffusion Coefficients from Analysis of Data on Kinetics of Coarsening

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It has generally been assumed that terminology "diffusion-controlled coarsening refers to the diffusion of solute in the majority (matrix) phase, with no distinction made between tracer, intrinsic and chemical diffusion. Indeed, analysis of data on coarsening of γ' (Ni_3Al) precipitates in a Ni-Al solid solution yields diffusion coefficients that agree exceptionally well with data on tracer diffusion of Al extrapolated from very high temperatures. The same is true for data on diffusion and coarsening in binary Ni-Ti alloys. At least in Ni-Al alloys the agreement is probably not surprising because chemical diffusion in the Ni-Al solid solution is not too strongly dependent on composition. However, the same kinds of analyses of data on coarsening do not produce comparably good agreement in Ni-Si and Ni-Ge alloys. In the latter system the data on coarsening are clearly in much better agreement with data on chemical diffusion. The same is true for data on the coarsening of γ (disordered Ni-Al) precipitates in ordered γ'. Here there can be no doubt that chemical diffusion prevails. In this talk older data will be reviewed and re-analyzed, and new data on diffusion coefficients obtained from the kinetics of coarsening of γ precipitates in a γ' matrix will be presented. The activation energies in this case are in extremely good agreement with data from conventional experiments on chemical diffusion in Ni_3Al.

Nuclear Magnetic Resonance and Impedance Studies of Diffusion in Nanocrystalline Ceramics

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The capabilities of nuclear magnetic resonance (NMR) and impedance spectroscopy (IS) to study diffusion and ionic transport [1] have increasingly been employed in recent years also for nanocrystalline materials, i.e. polycrystals with average grain sizes typically in the range from 5 to 50 nm and a correspondingly large fraction of interfacial regions of up to 50 vol% [2]. We report on recent NMR and IS studies performed by our group on non-metallic inorganic materials. Whereas NMR relaxation, lineshape and echo techniques give access to microscopic diffusion parameters like atomic jump rates and local barrier heights, IS was mainly used in the low-frequency limit to probe long-range ionic transport.

Nanocrystalline ceramics were prepared by high-energy ball milling or by inert gas condensation. Single-phase ion conductors (Li^+ or F^-) as well as nanocrystalline composites with an ionic insulator as the second phase were studied. In nearly all cases the diffusivity is dominated by the interfacial regions. Comparison of the NMR with the conductivity results showed that in particular the interfaces between hetero-phases are fast-diffusion pathways in the nanocomposites which suggests a possible route to design, e.g., solid Li electrolytes. Furthermore, comparison of the nanocrystalline with the corresponding microcrystalline and, in some cases, the amorphous counterpart materials yielded information on the volume fraction and the microstructure of the diffusion pathways.

[1] *Diffusion in Condensed Matter – Methods, Materials, Models*
P. Heitjans, J. Kärger (Eds.), Springer, Berlin 2004
[2] P. Heitjans, S. Indris, J. Phys.: Condens. Matter **15** (2003) R1257

Diffusion and segregation in nanomaterials

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Experimental measurement data on atomic diffusion in nanocrystalline materials are still very scattering while, till 25 years, grain boundary diffusion in conventional polycrystals can be measured with a good reproducibility (10-20%) at least in metals and metallic solid solutions.

This contribution makes an attempt to compare atomic diffusion in nano-crystalline materials and in their coarse-grained polycrystalline counterparts. The most important parameters which must be well known to make the results reliable (pre-annealing, chemical composition, diffusion regime.. .) are briefly discussed by using some examples recently published for coarse-grained polycrystals. Then, looking at the various data concerning nano-materials, we show that the value of diffusion coefficients and thus the nature of GBs depend on the technique applied for the synthesis of the material more than on the grain size:

- When it is possible to compare nano/coarse grain samples where GBs are near to an equilibrated state from the structure and the chemical composition point of view (metallic thin films), the grain size does not affect the grain boundary diffusion coefficients value.
- In presence of some porosity, diffusion can be close to surface diffusion.
- In samples synthesized by means of severe plastic deformation, the grain boundary diffusion coefficients (which are some order of magnitude higher than those in classical polycrystals) decrease as a function of pre-annealing treatments.

Some open issues of atomic diffusion in nanomaterials are pointed out and prospective topics of future research in this field are proposed.

Diffusion and Free Volumes in Nanocrystalline Materials

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Since the pioneering work performed on nanocrystalline materials twenty years ago, diffusion in these novel types of materials has attracted permanent interest, largely because material transport belongs to the group of physical properties differing most in nanocrystalline materials in comparison to their coarse-grained or single-crystalline counterparts.

An overview will be given on atomic diffusion in nanocrystalline metals and alloys [1] focussing on structurally stable, soft-magnetic nanocrystalline (n-) $Fe_{90}Zr_7B_3$ [2] and $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ as well as on hard-magnetic nanocrystalline $Nd_2Fe_{14}B$ [3]. Diffusion in these materials is of technical relevance for the formation of magnetic anisotropy which is induced upon annealing under mechanical load or in an external magnetic field. The diffusion studies were performed without any influence of residual porosity, structural relaxation, or grain growth. In the case of n-$Nd_2Fe_{14}B$, self-diffusion in liquid intergranular films, which are formed for Nd-rich compositions at high temperatures, could be studied [3].

Since diffusion is highly correlated with the presence of atomic free volumes, the results are discussed in the context with positron annihilation studies of thermal vacancy formation and interfacial free volumes of nanocrystalline materials. Recent progress in the chemically sensitive characterization of interfacial free volumes will be presented [4].

[1] R. Würschum, S. Herth, and U. Brossmann,
Adv. Engin. Mater. **5** (2003) 365
[2] S. Herth, M. Eggersmann, P.D. Eversheim, and R. Würschum,
J. Appl. Physics **95** (2004) 5075
[3] S. Herth, Feng Ye, M. Eggersmann, O. Gutfleisch, and R. Würschum
Phys. Rev. Letters **92** (2004) 095901-1
[4] S. Herth, H. Rösner, A.A. Rempel, H.-E. Schaefer, and R. Würschum
Z. Metallkd **94** (2003) 1073

Electron Probe Microanalysis in the Study of Diffusion in Thin Solid Coatings

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The possibility of the determination of diffusion profiles in thin coatings (below about 1 micron) by nondestructive x-ray microanalysis will be presented. Correction methods of the measurements are based on the analytical in-depth x-ray distribution functions and need to measure of the intensities of characteristic x-ray lines emitted from the sample at various accelerating voltages. During the measurements the electron beam impinges on the surface of the coating. The determined concentration profiles in the diffusion zone are obtained usining the "trial and error" procedure as a result of the agreement between the measured and calculated relative intensities of the analyzed x-ray lines.

The possibilities and limitations of the methods will be discussed. There will be shown, that the methods describe well the concentration profiles only in the studies of multiphase diffusion, when the concentrations change sharply at the boundaries of the formed phases. When the concentrations of elements in the diffusion zone change continuously, their profiles can only be described approximately as 3-4 sub-layers of different concentrations.

Some examples of the application of electron probe microanalysis in the study of diffusion processes in thin coatings will be shown.

Ternary interdiffusion coefficients in chosen Ni_3Al-based alloys

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A new modification of Dayananda's method was proposed that enables an evaluation of concentration dependence of diffusion matrix elements, $\widetilde{D}^{(Ni)}_{ij}$, using one diffusion couple only. The procedure is applied to interdiffusion in γ'-Ni_3Al-X (X = Cr, Fe, Nb, Ti) in temperature interval 1173 – 1533 K. It was found that activation enthalpy, $Q^{(Ni)}_{XX}$, and frequency factor, $D_o^{(Ni)}{}_{XX}$, decrease with increasing concentration of element X. In the limit $c_X \to 0$, the values of $\widetilde{D}^{(Ni)}_{XX}$ approach the literature values of tracer diffusion coefficients of X in Ni_3Al. An estimation of Al "tracer" diffusion coefficient in Ni_3Al was obtained that is in reasonable agreement with other estimations in the literature. With decreasing concentration of X in Ni_3Al, the difference between Arrhenius parameters $Q^{(Ni)}_{XX}$, $D_o^{(Ni)}{}_{XX}$ and respective values of $Q^{(Ni)}_{AlAl}$ and $D_o^{(Ni)}{}_{AlAl}$ decreases. $Q^{(Ni)}_{XX}$, $D_o^{(Ni)}{}_{XX}$ agree with values reported in the literature for very diluted solution of X in Ni_3Al.

Electromigration in Very Large Scale Integration of Interconnects

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On a piece of silicon chip of the size of a fingernail, we can make hundred millions of transistors. The chip is the key building block of modern microelectronic devices. To function together, the transistors must be interconnected by ultra-fine aluminum or copper wires having a diameter of one hundredth of our hair. These wires are called interconnects and they carry a very high electric current density. During device operation, the high current density can cause atomic displacement in the wire and lead to void (open) and extrusion (short) formation. The displacement is called electromigration and it is the most serious and persistent reliability problem of microelectronic devices and computers. The interconnects are 3-dimensional and are insulated by ultra-thin glass. The insulation induces thermal stress between the wire and the insulation. The 3-dimentional structure induces current crowding when the interconnect turns, which enhances electromigration. In this talk, the effect of current crowding on electromigration, the interaction between electromigration and stress, and the interaction between electromigration and chemical reactions in interconnects will be presented.

Radiotracer Diffusion and Ion Conduction in Polymer Electrolytes

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The paper deals with fast ion transport in fully amorphous polymer electrolytes which are synthesized by dissolving an inorganic salt in a polymer matrix. This class of soft condensed materials has practical importance as charge conducting medium in batteries, fuel cells, electrochemical sensors, etc. In fact, the Li-ion battery in modern laptop computers and mobile telephones is based on closely related materials. The paper not only reviews early diffusion research on polymer electrolytes but also presents new data resulting from recent studies by the Münster group.

We investigated ion transport in two different polymer electrolytes, one based on pure poly(ethylene oxide) (PEO) as polymer matrix, the other on a cross-linked random co-polymer consisting of PEO and poly(propylene oxide) (PPO). To this aim we performed not only radiotracer diffusion experiments for both cations (sodium) and anions (iodine) but also electrical conductivity measurements using impedance spectroscopy. Comparing the individual contributions of either ion species with the overall charge transport over a wide temperature range points to the occurrence of neutral ion complexes in the electrolytes. Fitting simultaneously all experimental data within an ion-pairing model yields accurate values for the diffusivity of either single-ion species, the diffusivity of ion pairs, the ion-pair binding energy, and the reaction constant of ion association/dissociation. The consequences and predictions of the model will be discussed, also in the light of some long-standing controversies about the mechanism of ion migration in polymer electrolytes. Some important keywords in this context are: Arrhenius or Vogel-Tamann-Fulcher behaviour, hopping or liquid like motion, and cation/anion transference numbers.

Self-organization of Semiconductors (Si, Ge) on Metallic Surfaces

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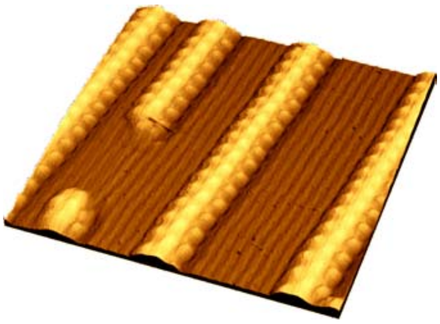
The formation of "surface alloys" confined near the surface can be observed not only during the growth of a thin film (generally deposited at low temperature) but also during the film dissolution process (at higher temperatures). When the deposited element and the metallic substrate present very different atomic and electronic structures, the nature of the surface alloys formed are strongly dependent on the surface orientation.
The aim of this talk will be to present a recent study of the formation of surface alloys in the special and unusual case of a semiconductor (Si, Ge) on a metallic surface (Ag(001), (111) and (110)). We will show a set of novel and surprising results obtained with several complementary techniques used in a synergetic way : (AES, LEED, STM and SXRD). Due to the confinement near the surface, silicon and germanium form in some cases astonishing nanostructures and in all cases original chemical and physical properties.



STM images showing silicon nanowires obtained on Ag(110) at room temperature (12.1x12.1 nm^2)

Grain Boundary Segregation versus Precipitation in Grains. Effect on Diffusion.

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The competition between grain boundary (GB) segregation and precipitation in grains in binary polycrystals, with limited solubility is well known but still not clearly understood phenomenon. If the solute concentration (X_i) in the grains is lower than solubility (X_{i0}) there is no precipitation in the grains, meanwhile the equilibrium between solute in the grains and in GB is obtained and the chemical potentials are equal: $\mu_i = \mu_i^{GB}$. When X_i approaches X_{i0} triple equilibrium must be riched, between GB segregation phase, saturated solution in the grain and precipitate (chemical compound, solid solution with different concentration, pure component).

It is clear that $X_{i0} < X_i^{pH}$ (X_i^{pH} is solute concentration in precipitate) but X_i^{GB}, solute concentration in GB segregation phase, according to the McLean segregation isotherm, may be as close as possible to the saturation value (X_{i0}^{GB}) if the enrichment coefficient b >>1.

The first question is how X_{i0}^{GB} is connected with X_i^{pH}. The second question is the effect of the competition under question on solute diffusion, both bulk and GB.

Evolution of Ultra Thin Metallic Deposits (Diffusion, Segregation) and Surface Alloys

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Dissolution of ultra thin deposits provides a means to determine the bulk diffusion coefficient and surface segregation parameters using surface sensitive techniques (via the measurement of the surface concentration Cs). From a structural point of view, LEED is the most used technique, but nowadays STM is often used to observe structural details at an atomic scale.

In the present study, Auger Electron spectroscopy (AES), LEED and STM were used to study ultra thin films evolution as a function of time.

Two type of systems are studied: total mutual solubility systems [Ag(Pd)] and tendency to order systems [Cu(Sb)].

Sb/Cu(111): Owing to the limit of solubility of Sb in Cu (3 to 4 at.%) and the extrapolated diffusion coefficient of Sb in Cu, the dissolution of one ML of Sb should not take more than a few seconds. The kinetics of dissolution shows a very different behaviour. At the very beginning, a fast dissolution is observed (which is normal) and then the dissolution is blocked on a plateau. This plateau corresponds, according to LEED observations, to an atomic structure of p(√3x√3)R30. STM measurements have been carried out to know if Sb atoms are in adatom position or in substitutional sites in the Cu(111) lattice.

Pd/Ag(111): This system is similar to the Ni/Cu(111) system previously studied (the diffusion coefficients have a strong concentration dependence). The very first results concerning dissolution of 3 to 8 Pd layers deposited onto a Ag(111) system will be exposed and discussed.

Hydrogen Diffusion, Embrittlement and Delayed Hydride Cracking in Zirconium Based Alloys

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The presence of hydrogen in metals and alloys can result in their embrittlement and delayed hydride cracking (DHC). This problem is very important for zirconium alloys operating in nuclear plants with high-temperature water environment as a coolant. The process of DHC comprises the following steps.

Hydrogen migrates in solid solution (α-phase) up the tensile stress gradient and accumulates near the crack tip. When its concentration exceeds the terminal solid solubility, the brittle hydrides precipitate normally to the applied stress. As a result, specific composite α+δ containing the plastic metallic α-phase and brittle hydride δ-phase will form in the crack plane. When the crack-tip hydride attains the critical length and thickness the local toughness of material is reduced to the level of the applied stress intensity factor. The crack tip advances through the embrittled region to be arrested by the ductile matrix. The process repeats itself in a step-by-step manner, resulting in slow crack growth.

Here, we present a new calculation model of DHC developed on the basis of steady-state solution of the known phenomenological diffusion equation. The steady-state velocity of DHC was prognosticated in Zr–2.5Nb alloy with different hydrogen content (25–100 wt. ppm H). It was observed that the calculated velocity obeys the Arrhenius law with activation energy of 58650 J/mol. The estimated threshold temperature for DHC depends on hydrogen content and increases from 205^{0}C (25 wt. ppm H) to 305^{0}C (100 wt. ppm H). As shown, the predicted DHC velocity and activation energy data are in excellent agreement with the known experimental ones.

Parameters Affecting the Oxidation Limited Lifetime of Thin Walled FeCrAl Components

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Alumina scales formed on FeCrAl-alloys during high-temperature oxidation protect them from corrosion degradation. For thin walled FeCrAl-components, a critical Al-depletion due to the scale formation may occur, which leads to breakaway oxidation of Fe and Cr. The oxidation rate, which largely determines the Al-depletion is significantly affected by the minor alloy composition. It depends on concentrations of the reactive elements, such as Y and Zr, which alter the diffusion processes in the scale by modification of the oxide microstructure and grain boundary composition. RE-incorporation into the alumina scale can in turn be affected by depletion of their very limited alloy reservoir and especially by interaction with common alloy impurities, such as C, N and P. At temperatures of around 900°C, formation of fast growing metastable Al_2O_3 can significantly shorten lifetime of thin walled components. The detailed knowledge of the oxidation kinetics and diffusion processes in the scale is required for a reliable lifetime prediction. Incorrect kinetics description can lead to significant lifetime underestimation.

Oxygen diffusion in doped polycrystalline alpha-alumina. Influence of grain size and dopant amount.

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Grain-boundary Oxygen diffusion in Yttrium, Scandium and Titanium doped polycrystalline Alumina is investigated. Since the solubility of these elements in the alpha-alumina grains is low, the doping elements are present in grain boundaries either segregated or precipitated. For this reason, oxygen mobility in the grain boundaries depends on their amount in the grain boundaries. Doped materials are obtained either via a nitrate route (Y or Sc) or an isopropoxide one (Ti). Two amounts of doping elements are chosen: 100 ppm and 1000 ppm. Various grain sizes are obtained by changing the heat treatments. After a hot isostatic pressing which gives very dense materials, samples are pre-heated in a ^{16}O atmosphere before diffusion treatment (1200°C, 1100°C, 1000°C). ^{18}O is introduced in alumina by ^{16}O/^{18}O isotopic exchange method. Diffusion profiles are obtained in a CAMECA IMS 4F SIMS device. The diffusion profiles show that oxygen is less present in the grain-boundaries for the Y-doped material, especially at the lowest temperature. This can correlated with the fact that yttrium is the less soluble than Sc or Ti, due to the high value of its ionic radius. Precipitates of yttrium-aluminium garnet (YAG) block the oxygen diffusion, particularly at low temperature (1000°C). The evaluation of lattice diffusion coefficients values is not very easy, due to the low penetration depth in the bulk and thus the values of diffusion coefficients in grain boundaries are given with care.

Diffusion of Oxygen and Gallium in Langasite

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Langasite ($La_3Ga_5SiO_{14}$) is a promising material for high-temperature piezoelectric applications significantly exceeding the operation limits of quartz. Therefore, high-temperature microbalances and gas sensors based on bulk acoustic waves (BAW) are feasible [1].

Since langasite does not undergo phase transformations up to the melting temperature of 1470 °C, the operation temperature range may, in principle, be extended up to the melting point. However, with increasing temperature the resonator quality factor decreases and limits the maximum operation temperature. Since the quality factor is related to the bulk conductivity, the kinetic mechanisms controlling electronic and ionic transport are the key issues for designing better materials.

This paper focuses on the understanding of the defect chemistry and the transport mechanisms which are essential to minimize the conductivity by application of appropriate dopants or substituents. In particular, the role of dopants and the diffusion kinetics controlling the ionic transport in langasite are evaluated and discussed. The authors present results of their investigations on oxygen and gallium diffusion in single and polycrystalline langasite, as well as different techniques used to obtain the diffusion data.

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Defects and Diffusion in Polycrystalline d-AlNiCo-Quasicrystals – Application of Mechanical Spectroscopy

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Measurements of internal friction, i.e. mechanical spectroscopy, allow to study the properties of anisotropic point defects. Stress-induced reorientation of the defects is connected with local atomic jumps which can be, in special cases, the elementary step of long range diffusion.

Internal friction measurements were applied to d-AlNiCo quasicrystals for compositions ranging from $Al_{72.8}Ni_{7.5}Co_{19.7}$ to $Al_{71.1}Ni_{18}Co_{10.9}$. The measurements were carried out in the temperature range from 290 K up to 1220 K for measuring frequencies between 1Hz and 10 kHz. A loss maximum of Debye type is observed at ≈ 700 K (2Hz) for both the I-state and the bCo-state. The peak is not present in the 5f-state. From this we conclude that there exists an atomic configuration in the I-state and in the bCo-state which is not present in the 5f-state. The activation enthalpy of the peak of H = 1.9 - 2.2 eV is in the range of values obtained from tracer diffusion experiments. The peak is attributed to local atomic rearrangements which occur with the same atomic jumps as long-range self diffusion.

A high temperature a viscoelastic damping background is observed for all investigated states (5f, bCo and I) above 800K (2Hz). The slightly higher activation enthalpy of the background (H = 2.4 – 3 eV), compared with diffusion experiments, can be explained by interation of moving dislocations with point defects, e.g. phasons.

The Nonlinear Interplays of Mechanical and Chemical Strains in Diffusion

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An elastic crystal is characterized by a set of crystal-structure parameters that may be expressed in terms of three edge lengths and three interaxial angles, in addition to its anisotropic elastic moduli. For some alloy crystal structures, a composition can vary from the stoichiometric value without altering the type of structure, although the edge lengths and interaxial angles change somewhat with composition. This fact may be quantified into the statement that the crystal structure of a multi-component alloy is a function of the local concentrations. Thus, nonuniform concentrations lead to a nonuniform crystal structure, which, in turn, generates a state of geometrically necessary eigentransformation as well as an associated state of elastic transformation. The elastic transformation defines the (traditional) stress-associated elastic deformation, which is well understood in classical continuum mechanics. The eigentransformation is a direct result of the nonuniform composition and may, therefore, be interpreted as a chemical deformation. The product of the (traditional) stress and the deformation rate is the density of working in classical continuum mechanics. It is shown in that the product of a generalized energy momentum tensor and the aforementioned eigentransformation rate also contributes to the density of working. For this reason, the energy momentum tensor may also be termed a chemical stress, in addition to being named a material or configurational stress. At the same time, the question whether the chemical potential for a solid should be a tensor or scalar becomes mute, as a part of the scalar potential is actually the product of two tensors. In forming the product however, the mechanical and chemical transformations are coupled in a nonlinear way, which is exploited in this paper to examine the nonlinear effects of mechanical stress on diffusion.

The “C” Factor in LeClaire’s Theory of Solute Impurity Diffusion

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LeClaire’s theory of solute impurity diffusion which utilizes valence differences between solvent and solute impurities gives the difference in diffusional activation energy between impurity solute and solvent, ΔQ, as $\Delta Q = \Delta H_2 + \Delta E - C$ where ΔH_2 and ΔE are calculated from valence differences between solvent and solute and the calculation of “C” requires the use of experimental values of the frequency factors for solvent and impurity diffusion. LeClaire’s theory was moderately successful in predicting the activation energy for diffusion of elements from groups III A, IV A and V A of the periodic table in the noble solvent metals Cu, Ag and Au. The theory was less successful in describing diffusion of the metals from groups VI B, VII B and VIII in the noble metals Cu, in that negative values for the valence of these impurity metals had to be assumed. LeClaire, however, had used the traditional valence of one for the noble solvent metals. Burachynsky and Cahoon modified the LeClaire theory by using the Engel-Brewer valences of three for face-centered- cubic materials, two for closed-packed-hexagonal metals and one for body-centered-cubic materials. They obtained reasonable agreement between experimental and calculated values of activation energy when the differences in zero-point energy between solvent and solute were also considered. However, they did not calculate values for the factor “C” since the experimental values of frequency factor are generally subject to large error limits resulting in widely varying estimates for “C”. The present paper includes values of “C” in the calculation of activation energy for solute impurity diffusion. Values of “C” are calculated for a number of impurity solutes in various solvent metals and it is assumed that “C” is a linear function of the valence difference between solvent and solute impurity. $\Delta H_2 + \Delta E$ and “C” are then functions of valence differences alone and values of activation energy for any solute impurity may be calculated.

Nonlinear Theory of Stress Induced Diffusion in Crystalline Solids

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The thermodynamics of stress diffusion in an anisotropic elastic material is considered. Departing from the geometry and kinematics of the lattice deformation induced by stress and chemical strains the respective equations for deformation rate are derived. The constitutive equation for the specific free energy takes into account the lattice strain, lattice curvature (dislocations), chemical concentrations and temperature. The equation admits the local minimum of crystal energy with respect to some values of chemical concentrations. The thermodynamic driving forces are derived from the energy balance by differentiation of the specific free energy function. Among others the driving forces for chemical diffusion and lattice curvature transport (dislocation movement) are obtained. The forces comprise both the osmotic and stress induced terms. The influence of crystal symmetry on diffusional anisotropy is considered. It is shown that for non-zero stress gradient the stress diffusion term can vanish with respect to a few reasons: e.g. with respect to the local minimum of crystal energy obtained for a given value of chemical fraction.

The surface energy is also considered. Departing from the balance of energy on a discontinuity surface the driving forces resulting from the differentiation of the bulk and surface energy are obtained. This leads to the thermodynamic relations between the energy distribution and the driving forces governing the grain boundary migration and surface tension.

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Software of Simulation of Oxidation Processes

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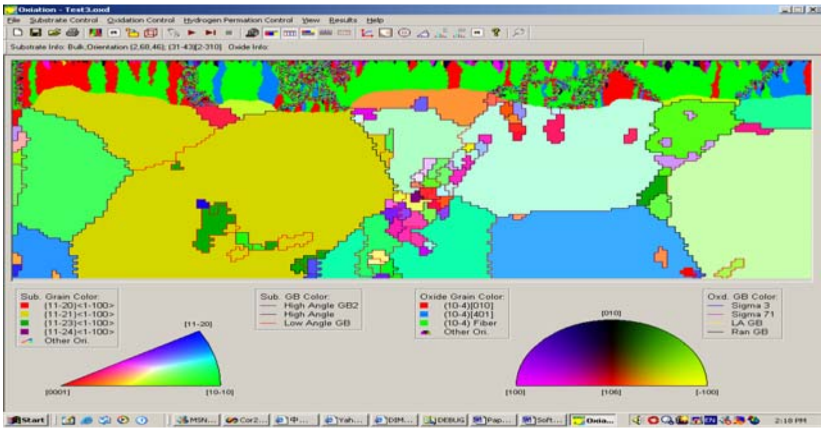
A discrete simulation methodology has been developed that incorporates many structural characteristics of polycrystalline material properties, such as, texture, grain boundary, microstructure, phase composition, chemical composition, stored energy, and residential stress. The computer models developed to study oxidation process are based on quantitative description of oxide and substrate structure. That description allows simulating the transport of metal and oxygen ions along interfaces and bulk portion of materials .The proposed model help researchers and engineers to understand physical mechanism of oxidation, predict material behaviour, and optimize material processing and properties.
In this paper, we will present the results of simulation results of oxidation process on different substrate of Zr-Nb alloys, which are used for manufacturing the pressure tube in CANDU nuclear reactors. The effects of substrate texture, microstructure, grain boundary, and beta phase distribution on oxidation kinetics and hydrogen permeation will be demonstrated.



Substrate Info: Bulk,Orientation (2,60,46); (31-43)[2-310] Oxide Info:

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Atom Jump Frequency in Compounds Measured Using Nuclear Quadrupole Relaxation

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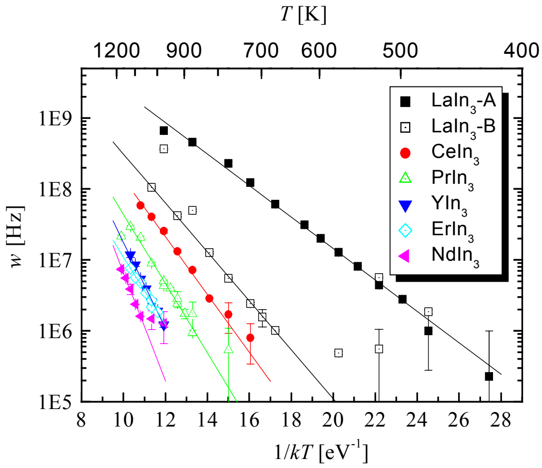
We have measured nuclear relaxation of ^{111}Cd tracer atoms jumping on the In-sublattice in In_3La [1] and In_3RE (RE= Ce, Pr, Nd, Er, Y), which all have the Cu_3Au structure, using perturbed angular correlation of gamma rays (PAC). For this sublattice, each near-neighbor jump leads to reorientation of the axis of the electric field gradient at the nucleus by 90°. Experimental perturbation functions were fitted using an exact stochastic model to obtain tracer jump frequencies. As will be shown, the jump frequency w determined using PAC is related to the diffusivity via $D = \frac{1}{12} f a^2 w$, in which f is the correlation coefficient and a is the lattice parameter. Results are shown in the figure, including two sets of jump frequencies for In_3La from measurements at more In-rich (A) and less In-rich (B) phase boundaries, which differ in composition by only about 0.1 at.%. As can be seen, set A has frequencies much greater than set B. Possible diffusion mechanisms will be discussed. This method is well suited for measuring atom movement at boundary compositions in “line” compounds provided there exists an EFG that reorients in each jump. Finally, we note that the correlation coefficient can be determined from simultaneous measurements of w and D.



[1] M.O. Zacate, Aurélie Favrot and G.S. Collins, Physical Review Letters (accepted).

A diffusion-effusion database for ISOL-target improvements

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In the case of an Isotope Separation On-Line (ISOL) facility a crucial requisite for an efficient production of short-lived nuclei is the fast release and extraction of the radioactive isotopes produced in the target ion-source system. In order to take control over the variables that affect the design and development of these target matrixes, a database management system containing the relevant information in this diffusion effusion process contributing to the delay time has been built.

This Oracle database is constructed within an Open-URL framework directly reachable from any web-browser at http://www.targisol.csic.es. The user interface is designed in such a way that already the first time user will easily find the information searched for. The database includes the diffusion and effusion data of most elements in a range of materials. About 2400 entries are presently stored in the database.

This paper presents the database and the web application as a tool for diffusion-effusion studies. The structure of the database and the user interface are reviewed.

Approximate Solutions of Grain Boundary Diffusion Equations in the B_2 Regime

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Most of the mathematical treatments of grain boundary diffusion are based on the model of an isolated grain boundary, first proposed by Fisher [1]. To derive an approximate analytical solution he neglected the direct volume diffusion from the surface into the perfect crystal and the diffusion term $D\partial^2 c/\partial z^2$ with the statement: "Whenever the penetration of diffusing material is much greater in the slab than elsewhere, diffusion outside the slab is primarily normal to the slab ...". Furthermore, Fisher's numerical calculations showed that after very short time the grain boundary diffusion is quasi-steady in the slab (i.e. the grain boundary), which means that the partial time derivation $\partial c_b/\partial t$ can be omitted. These approximations are valid in the so called B_2 regime, a classification proposed by Mishin and Razumovskii [2], which is often practically fulfilled.

It is well known that exact solutions of the grain boundary diffusion equations in the B_2 regime are simplest in the reduced variable w. Our proposed method to derive approximate solutions is based on the assumption that by means of a non-linear coordinate transformation $v = v(w)$ the grain boundary diffusion problem can be approximately reduced (at least in most practically used ranges of w) to the problem to solve an ordinary differential equation. Fisher's attempt to solve the problem approximately can be considered as a special case if one assumes that a linear coordinate transformation, $v = w$, is sufficient to get reasonable approximate solutions. We will derive an appropriate non-linear coordinate transformation and will consider the case of an infinite sample as well as a thin film.

[1] J. C. Fisher, *J. Appl. Phys.* **22** (1951), 74.
[2] Yu. M. Mishin and I. M. Razumovskii, *Acta Metall. Mater.* **40** (1992), 597.

Computer Simulation of Precipitate Evolution in Multicomponent Metal Alloys

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A new method has been suggested for numerical simulation of diffusion-controlled evolution of a polydispersed precipitate ensemble in a multicomponent metal alloy. The algorithm is based on the mean field approach and the consideration of diffusion in field cells. Equal component concentrations on boundaries of all cells are assumed. The finite difference method is used to calculate concentration distributions in field cells.

The abilities of the suggested method are analyzed. It's demonstrated that it has much more facilities in comparison to the existing ones and enables to simulate precipitate evolution in two-phase alloys at all its stages. Diffusion in particles and nucleation of the new ones can be taken into account as well.

Numerical realization of the worked-out method in form of a computer program has been accomplished and calculations of precipitate evolution in steels of different composition at different stages have been carried out. Comparison of calculation results including particle size distributions to the available experimental data for different stages of precipitate evolution has shown their good agreement (Fig. 1).

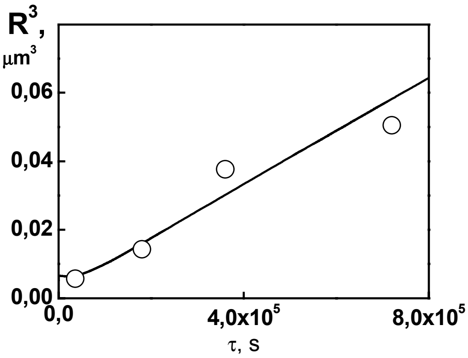

Fig.1. Comparison of calculated and experimental temporal dependences of VC particle size in a steel at 1100^0C annealing

Modelling of phase transformations in substitutional alloys

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To simulate diffusional phase transformations it is necessary to solve the coupled problem of bulk diffusion and interface migration. The solution of diffusion equations makes it necessary to know the boundary conditions at the surface of the system and the contact conditions at the migrating interface. Usually it is assumed, that the system is closed, and no fluxes exist on the surface of the system. One class of the contact conditions at the migrating interface stems from the mass conservation law. It relates the jumps in the fluxes across the interface, the jumps in concentrations and the interface velocity. Unfortunately, these contact conditions are not sufficient, and additional conditions are required to solve the coupled problem. Therefore, further contact conditions are usually added, e.g. the ortho-equilibrium conditions prescribing the continuity in chemical potentials of all components across the interface. However, the ortho-equilibrium contact conditions imply no driving force at the migrating interface, which means a deliberate assumption of the infinite interface mobility. A more general set of contact conditions restricts the continuity in chemical potentials only to the interstitial elements and allows jumps of the chemical potentials of the substitutional elements which, however, are assumed to be identical for all substitutional elements. This set of contact conditions at the migrating interface for the multi-component systems makes it is necessary to solve a set of complex non-linear equations before every time integration step. This may be a difficult task which may cause some solution instabilities.

To overcome such difficulties one can engage Onsager's thermodynamic extremal principle of maximum dissipation with the fluxes of the components and the interface velocity being the quantities with respect to those the dissipation is maximized.

Kinetics Lecture Modules

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Diffusion in solids, kinetics, solidification, and crystal growth are broadly applicable subfields of materials. Teaching modules for materials science were introduced at Rensselaer Polytechnic Institute, in the fall semester 2000 for the subject of Diffusion in Solids. These modules were published on our Departmental website in Spring 2002. This past year we developed a series of “module sets” for the subject of kinetics. The modules, for ease of adoption by others, consist of stand-alone Microsoft files that succinctly present the content of each topic, adding commentary, animation, and emphases that go beyond the limits of printed notes and texts. Their topical content is selected on the basis of the books and original course notes already used to teach kinetics of materials. In addition, areas of conceptual, or mathematical difficulty encountered by students and known to us will be explicated, and appropriate comments and examples added to alert students and instructors.

We assembled 26 stand-alone PowerPoint© lecture modules, 8 original movies, 3 Excel-Visual Basic© spreadsheets plus numerous exercises to be solved by students in class. The modules contain, where appropriate, parts of original class projects submitted by RPI students as a requirement. Some of the implementations refer to the historical discoveries by A. Fick, some refer to library searches for systems exhibiting spinodal behavior. Other students offered solutions to the Boltzmann-Matano inversion of diffusion data using software packages such as Excel©, Maple© or Mathematica©. The most skilled students took the challenge and developed movies based on finite element codes (MatLab©), movies based on molecular dynamics modeling, and, finally, random walk simulations (Monte Carlo simulations). Other sources that we found useful for completing these educational modules derive from documents shared with other scientists as well as internet selected sources.

Software for Simulation of Diffusion Process in Polycrystalline Material

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Understanding of diffusion processes in polycrystalline solids is of great importance for studying processes like oxidation, precipitation, creep, superplastic forming, annealing and other. In this paper, we will introduce our latest commercial software that is able to simulate the diffusion process in poly and nano-crystalline solids. The diffusion process is simulated based on Random Walk theory. The diffusion matrix can be computer generated or obtained from the experimental measurement using Orientation Imaging Microscope. The software describes microstructure and incorporates the effects of the material's texture, grain size and shape, grain boundary character distribution, statistical information on CSL boundary distributions, contribution from triple junctions and interfaces, incorporate the trapping of diffusing atoms and a role of second phases on the diffusion process. A built-in database of diffusivities of various diffusing species and the user friendly interface make the software easy to use. The output of simulation can be presented as a normalized concentration profile, a two-dimensional contour map of diffusing species, and in many other useful statistical representations.

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Bi and Pb Surface Diffusion on Polycrystalline Cu Studied by Scanning Auger Microscopy

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No study has reported thus far on the meeting of two adsorbed layers of different elements which spread towards each other to form a two-dimensional diffusion couple. Here, we study adsorbed Pb and Bi on polycrystalline Cu in a scanning Auger microscope at 473 K *in situ* (fig. 1). This follows surface diffusion studies of one of us* on these systems using different setups.

We observe a drift of the line where the two adsorbed layers meet, in the direction of the Pb covered surface, which results from a stronger adsorption of Bi on Cu than of Pb on Cu. Superimposed on this drift, the adsorbed Bi and Pb intermix over a region which widens with time. The interdiffusion of the components has been interpreted by the Boltzmann-Matano model.

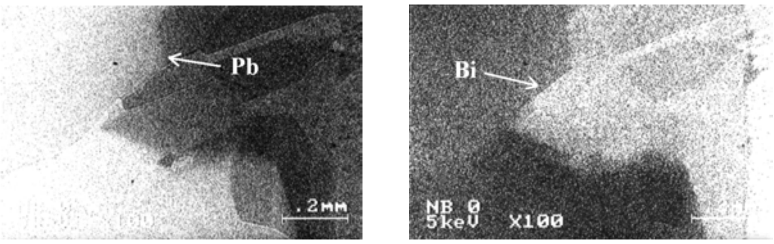

Fig. 1. Auger maps at 473 K of the same zone: Pb (left), Bi (right). The Pb and Bi adsorbed layers meet along a boundary which widens with time.

*Moon, J., Wynblatt, P., Garoff, S., Suter, R. *To be published in Surface Science*

Sedimentation of Substitutional Solute Atoms in Intermetallic Compound of Bi-Pb System under Ultra-Strong Gravitational Field.

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Ultra-strong gravitational field can induce sedimentation of even atoms in condensed matter. We had realized sedimentation of substitutional solute atoms in some miscible alloys. In this study, the ultra-centrifuge experiments were performed on an intermetallic compound of Bi-Pb system (Bi_3Pb_7) by changing the experimental conditions of the sample size and time duration (experimental conditions; maximum centrifugal force: $1.0x10^6$g level, temperature: 130-150 □, duration: 30-150h, state: solid). Composition changes were observed in the centrifuged samples. It was found that the Bi phase appeared from starting state of Bi_3Pb_7 around the weak gravitational field region of the sample. These results showed that sedimentation of substitutional solute atoms occurred and induced the decomposition in intermetallic compounds.

Self-defects in a Silica Glass, a First-principles Study

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SiO_2 in its crystalline or amorphous phases is a key material in a variety of scientific and technological fields as for example microelectronics devices or nuclear glasses. SiO_2 can be exposed to radiations which affect its physical properties. The understanding of the defects formation and migration seems crucial in order to predict the behaviour of this material in a radioactive environment. Furthermore, the formation energies of the defects can't be easily determined by experiments, so it is important to calculate them by numerical methods.

Earlier works (ref. [1], [2] and [3]) have shown the different structures of the oxygen vacancy for different crystalline polymorphs and for 72 atoms amorphous super-cells. Here we present a complete and statistical first principles study of self-defects in an amorphous 108 atoms SiO_2 super-cell. The ab-initio calculations were performed using independently the VASP, SIESTA and PWSCF first principles codes based on density functional theory (DFT) within the local density approximation (LDA). As expected, at variance with SiO_2 crystalline phases, the defect formation energies show certain distribution, because defect sites are non-equivalent in the glass. We will discuss how this non-equivalence and its relation to the formation energy distributions may be interpreted, on a quantitative basis, using some local properties of the initial configuration or of the defect precursors. We prove that the formation energy dispersion is correlated to the local pressure before the defect formation. Finally we will present the principal diffusion mechanism as a function of the oxygen partial pressure and his activation energy.

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2. N. Capron, S. Carniato, G. Bourreau and A. Pasturel, J. Chem. Phys 112, 9543 (2000).
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The Effective Interdiffusion Coefficients in Experimental Investigation of Interdiffusion in Ternary Systems

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The pecularities of using effective interdiffusion coefficients for describing the interdiffusion process in ternary systems are considered. It is shown that the effective interdiffusion coefficients are directly related to the diffusion path developed in a given diffusion couple and the corresponding relationship between these values is derived. Some special cases are also considered. Results of calculation of the diffusion path for several diffusion couples in the ternary systems Co-Ni-Fe and Cu-Ni-Fe are presented. It is shown that calculation of concentration profiles using Boltzmann's solution for diffusion equation together with effective interdiffusion coefficients can be carried out easily even in the cases when one of the effective interdiffusion coefficients has singular points, i.e. when zero-flux or zero-concentration-gradient planes for one component develop in the diffusion zone.

Some specific properties of effective interdiffusion coefficients and their dependence on coordinate in ternary diffusion zones are discussed.

Ab-initio Study of the Stability and Mobility of Self-interstitials and Small Interstitial Clusters in α-Fe

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We report a detailed study of the stability and migration mechanisms of self-interstitial atoms (SIAs) and small SIA clusters in α-Fe. Because of the discrepancies between empirical potential results and experiments, in particular on the SIA migration energy, this study is performed at the *ab initio* level with the SIESTA DFT code, which uses localized basis functions. We have first validated our calculation method on bulk and vacancy properties by comparison with plane-wave calculations. Using supercells of 128 atoms, we have then investigated the relative stability of various SIA or SIA-cluster configurations and determined the full transition pathways for a series of migration jumps or on-site rotations using a constraint relaxation technique.

In agreement with experiments we find the <110> dumbbell to be the most stable SIA configuration with a migration energy of 0.34 eV. The migration mechanism is identified to be the nearest-neighbor translation-rotation jump. The <111> dumbbell is found to be nearly unstable. The second nearest-neighbor jump is proposed as complementary migration mechanism with migration energy 0.50 eV. The SIA on-site rotation activation energies are larger than the migration energy showing that the experimental value of the rotation energy corresponds to the rotation-translation energy. The stable configuration of di-SIAs is made of nearest-neighbor parallel <110> dumbbells. The migration mechanism is similar to that for SIAs, with simultaneous or successive translation-rotation jumps of the dumbbells; the migration energies are practically the same in both cases, i.e. 0.42 eV. This value is in quantitative agreement with the experimental value of the activation energy attributed to the migration of small SIA clusters at stage II in resistivity recovery experiment, attesting that di-SIAs are at least some of these clusters. Finally, the first results on the relative stability of various configurations of larger SIA clusters and their migration mechanism are also discussed.

Diffusion of Al in Fe in the Alternating Magnetic Field

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The problem of the influence of the alternating magnetic field (AMF) on impurity diffusion is the least investigated. There is a hypothesis, that the AMF should render the appreciable effect, however this phenomenon has not yet been studied experimentally. In the present work the results of measurements of this effect executed by a radiographic method are reported.

Diffusion occurred from thin layers of Al which were deposited by thermal evaporation in vacuum on plane faces of cylindrical samples of Fe with the grain size 1-2 mm. Diffusion annealings of 4-17 h are executed in vacuum 10^{-5} Tor in and without AMF. Frequency dependences of diffusion coefficients (DC) of Al in Fe are measured at temperature 730 °C in AMF with amplitude of 79,6 кA/m and frequency 0.2, 0.5, 1.0, 2.0 and 5,0 Hz. Temperature dependences are investigated at temperatures 700, 730, 745, 760, 780°C and the fixed frequency 1Hz of AMF. In parallel, measurements were conducted on control samples in identical conditions without imposing AMF.

The results of the measurements show, that in the investigated interval of frequencies relative Al DC in Fe $D_{rel}=D(f)/D_{H=0}$, determined as a ratio of DC in AMF D(f) to the appropriate value without AMF $D_{H=0}$, depends non-monotonously on the frequency of an AMF field and surpasses it in 2,5-5 times. Temperature dependences have shown, that external AMF considerably influences the process of diffusion in a ferromagnetic domain of temperatures. In the paramagnetic domain of temperatures the effect of external AMF is absent.

Possible mechanisms of the influence of the AMF, connected with magnetostriction, interaction of moving domain walls of Fe with atoms of Al and dislocations are discussed.

Native Neutral and Charged Defects in Alpha-quartz: from ab-initio Calculations to Equilibrium Concentrations

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We present first principles calculations of the formation energy of silicon and oxygen vacancies and interstitials in alpha-quartz, in several charge states. We show structures of the defects, some of which are unknown, namely silicon defects and antisites.

Some specific features, like the effect of charge on the formation volumes as found by our calculations, will also be discussed. We take into account the influence of defect concentrations on the Fermi energy by solving numerically the equation imposing charge neutrality and we show the dependence of the Fermi energy and the resulting defect concentrations on temperature and oxygen partial pressure. We discuss the implications for oxygen and silicon self-diffusion in SiO_2 and for intrinsic ionic conductivity.

Numerical Study of Grain Boundary Diffusion in Nanocrystalline Materials

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Diffusion in nanocrystalline materials is becoming an increasingly important topic. The analysis of diffusion profiles obtained in nanocrystalline materials with enhanced grain boundary diffusion, however, is not straightforward since assumptions made in the deviation of type A and B kinetics are often not fulfilled. In this contribution numerical diffusion studies are performed in order to understand the specific behavior caused by the high density of interfaces in a nanocrystalline material. A continuum model based on 2D Fick's 2-nd law was solved by means of the finite element method. This allowed us to analyze the diffusion profiles for different geometrical situations such as an isolated boundary, parallel boundaries of high density and grains with grain size less than 50 nm. The analysis was carried out for different diffusion lengths corresponding to Harrison type A and type B kinetic regimes. For the isolated boundary a very good agreement was achieved in comparison with the classical Whipple's solution. For nanocrystalline grains, however, considerable error can occur when analyzing the effective diffusion profiles in the conventional Harrison type A and B kinetics. Depending on the applied conditions the error can amount to more than a factor of two. It is discussed how the geometrical parameters (density of grain boundaries, spatial orientation of grain boundaries), the different ratios $\Delta = D_{gb}/D_g$ and the diffusion time affect the error.

Theory and Simulation of Diffusion under Pressure

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The understanding of the effects of pressure on diffusion in solids is limited. Several years ago a new approach was suggested by us to resolve the problem of the influence of elastic stress on the vacancy jump rate for atomic diffusion in crystals [1]. A uniform pressure provides the simplest application of stress for checking the theory. The main characteristics of pressure influence on diffusion processes are formation and migration volumes, and the expressions for these volumes were obtained in the framework of the developed theory. Recently, using similar reasoning, we have built a general approach to calculate the activation volume for different mechanisms in solids. Based on it we have built an advanced model, which allows us to calculate migration volume for elementary diffusion jump for different jump types and different local atom environments. The value of the migration volume is very sensitive to the atomic structure in the nearest vicinity of a defect, which makes it necessary to consider a big amount of atoms in a model crystallite and to take into account an elastic matrix around the cell. If a diffusion coefficient can be expressed in terms of jump rates then, with the help of the developed model, we can evaluate the migration volume for each rate. In the case, when the mechanism is realized via several different types of atom jumps, Monte-Carlo simulation under different pressures is performed, using the previously calculated migration volumes for these jumps. Consequently, the dependence of diffusion coefficient on pressure in different systems and for different mechanisms is obtained.

1. A.V.Nazarov, A.A.Mikheev, Defect and Diffusion Forum,(1997) Vol **143-147**, p 177.

Vacancy properties and vacancy-carbon interactions in α-Fe and their impact on self-diffusion

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We have performed a detailed *ab initio* study of the energetics of vacancies in pure and carbon-doped ferromagnetic α-Fe using *ab initio* DFT-GGA calculations. The calculated values of the migration and formation energies, $E_m=0.63\pm0.05$ eV and $E_f=2.0\pm0.1$ eV, confirm that recovery stage III can be attributed to vacancies with $E_m=0.55$ eV and support the upper bound of experimental estimates of E_f. The migration path is single-bumped but very-flat. The vibrational modes for the stable and saddle-point configurations have been computed using the DFPT formalism. A low frequency mode, localized on the nearest neighbors of the vacancy, with tetrahedral symmetry has been identified. Large values are found for the vacancy formation entropy, namely 3.3 k_B, and the attempt frequency. We have also investigated the effect of electronic entropy and of ferromagnetic to paramagnetic transition.

We have then determined the equilibrium structures of vacancy-cabon complexes, VC_n (n=1, 6), where carbon atoms occupy one of the six octahedral sites around the vacancy. The V-C and VC-C interactions are found to be highly attractive (0.3 and 0.7 eV respectively). The effects of carbon on vacancy concentration and vacancy migration will be discussed. The high stability of VC_2 complexes changes the picture of the interpretation of various experiments.

From the technical point of view, these calculations were performed using the PWSCF plane wave code (in particular for phonons) and the SIESTA code (in particular for larger cells, i.e. up to 128 atoms). An emphasis was also put on the choice of the exchange-correlation functional (LDA or GGA), which was found to affect significantly the vacancy formation calculations.

Comparative ab initio Study of Point Defect Energies and Atom Migration Profiles in the $L1_2$-ordered Intermetallic Compounds Ni_3Al, Ni_3Ga, Pt_3Ga, Pt_3In

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In order to obtain a fundamental understanding of the kinetics of ordering in intermetallic compounds and in order to correctly interpret experimental measurements like electrical resistivity, one needs reliable values of defect formation and migration energies. Therefore formation energies of antisite defects and vacancies were derived for the $L1_2$-ordered intermetallics Ni_3Al, Ni_3Ga, Pt_3Ga, Pt_3In by a supercell ab initio approach. A thermodynamical treatment for point-like defects was then used for the calculation of temperature-dependent defect properties. In all cases antisite formation needs less energy than vacancy formation, the difference being larger (by 0.75-1.00 eV) in the Ni compounds than for the Pt compounds (by ~0.3-0.6 eV) considered in this study. For analysing the results, bonding properties were investigated by calculating elastic and equilibrium properties for the perfectly ordered compounds. Some of the tendencies observed can be made plausible by arguments of atom size and relative rigidity of the lattice. Energy profiles for atom jumps were calculated by statically displacing the jumping atom and relaxing the surrounding neighbours. The influence of variable atomic neighbourhoods on the migration barrier and the stability of the initial and final states were studied by systematically exchanging nearest and next nearest neighbour atoms.

Vacancy Concentrations in Silicon Determined by the Diffusion of Iridium into Silicon Wafers

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Vacancies (V) and self-interstitials (I) play an important role in diffusion doping and other high-temperature processes during silicon device fabrication. Whereas the transport coefficients of these native defects in silicon are known satisfactorily well, reliable data for equilibrium concentrations of V and I are still rather sparse. Earlier work by our group indicated that a detailed analysis of the diffusion behaviour of Ir in Si may provide information about vacancy properties in Si. This was based on the observation that Ir diffusion proceeds by interstitial-substitutional (i-s) mechanisms which comprise the kick-out mechanism involving I and the dissociative involving V. In particular, the sensitivity of Ir diffusion to V concentration can be understood from the circumstance that the (low) Ir solubility on substitutional sites and the equilibrium vacancy concentration are of the same order of magnitude over a range of suitable temperatures
Diffusion experiments were carried out between 875 and 1050 °C using Si wafers deposited with a thin Ir layer on both faces. Penetrations profiles were measured by means of neutron activation analysis in conjunction with mechanical sectioning. The large neutron capture cross section of natural Ir and the suitable half life of the ^{192}Ir isotope enabled us to detect extremely low Ir concentrations. Fitting of the profiles within the framework of i-s diffusion yields not only data for the frozen-in V concentration in the as-grown Si wafers but also for the equilibrium V concentration at the diffusion temperature. The present results will be compared with literature data and discussed in terms of vacancy formation enthalpy and entropy.

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Diffusion of Si in Ti_3Al Intermetallic Compound

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Ti_3Al is the intermetallic compound which has been known to be a potential material for high temperature structural application for about 30 years. Recently, this compound has received much attention as a conductive diffusion barrier between polycrystalline-Si and oxides in ferroelectric memory cells. However, there is no diffusion data of Si in Ti_3Al in the literature in spite of its importance for evaluating the property of the Ti_3Al as the diffusion barrier. Interstitial fast diffusion has been suggested for solutes with relatively small atomic radii such as Fe and Ni, while substitutional diffusion with the constraint to preserve the ordered structure is expected for solutes with atomic radii comparable to those of Ti and Al. It is interesting to examine the features and the mechanism of Si diffusion in Ti_3Al since the atomic radius of Si is smaller than those of Ti and Al but larger than those of the fast diffusers.

We studied the Si diffusion in Ti_3Al compounds with five compositions of 24.5at%Al to 34.7at%Al by using the diffusion couples (Ti_3Al/Ti_3Al-X; X=0.5at%Si) at 1248-1423K. The diffusion coefficients of Si, D_{Si}'s, were smaller than those of Ti and Al by a factor of 1/10 to 2/3 in the temperature range. The D_{Si}'s exhibited slight increase with Al concentration within the same order of magnitude. The activation energies of Si diffusion, Q_{Si}'s, evaluated from the Arrhenius plots were relatively close to those of Al diffusion, Q_{Al}'s, rather than those of Ti diffusion, Q_{Ti}'s, for corresponding Al concentration. The Q_{Si}'s were comparable to the calculated activation energies of the Si diffusion by the sublattice antisite diffusion (SAD) mechanism in which Si atoms substitute for Al-sites preferentially in Ti_3Al and diffuse via Ti-sublattice in the form of antisite atoms by exchanges with vacancies as well as Al atoms.

Diffusion of Hydrogen in Single-Phase and Two-Phase Beta Titanium Alloys

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Beta titanium alloys are very attractive materials for many applications because they combine low density, high strength and excellent corrosion resistance. Little information exists on hydrogen diffusivity, and the available data indicates a much higher hydrogen diffusion coefficient as compared to alpha and alpha+beta alloys. In order to predict the range of applicability of beta titanium alloys in environments which release hydrogen, the hydrogen diffusion coefficient D_H needs to be known quantitatively.

In the framework of this study two methods were applied to determine the value of D_M. One is based on electrochemical charging of half the length of long thin rods. After charging, the rods were annealed enabling hydrogen to diffuse. Hydrogen concentration profiles were evaluated on the basis of Matano technique, in order to reveal the effect of concentration on D_H. Another method applies continuous gravimetry which allows to control the weight increase of samples as a consequence of the uptake of hydrogen from He/H_2 gas mixtures.

The results obtained on several commercial beta titanium alloys documented that a strong effect of microstructure varied in a wide range in structural alloys and can be controlled by means of heat treatment. The values of D_H determined were correlated with the results of microstructural examination using optical and scanning electron microscopy.

In order to characterize the influence of single alloying elements on D_H, binary alloys of the systems Ti-V and Ti-Mo were studied at various contents of the respective alloying element. The concentration range represented the compositions commonly found in commercial alloys. A comparison of the values of D_H in commercial and binary alloys shows a strong effect of minor alloying elements and phase composition.

"Intrinsic" and "Impurity" Mechanisms of Volume Diffusion of Gold in Iridium Single Crystals

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Volume diffusion coefficients of gold in iridium single crystals (mono-Ir), which were annealed at a temperature from 1300 to 2000 K (0.48 to $0.75T_m$) in a ultra high (UHV) or technical-grade (TGV) vacuum, were measured by the method of secondary ion mass spectrometry (T_m is the melting point). The activation enthalpy $(Q_{SD})_{Ir}$ of the volume diffusion in iridium, which is used in calculation of the energy E_{vImpAP} of interaction between a vacancy (v) and an impurity atomic probe (ImpAP), coincided within the measurement accuracy with a linear dependence $Q_{SD}(V_{SD})$ of the self-diffusion activation enthalpy in transition d-metals located in the middle of the periodic table. Here $V_{SD} = 0{,}3T_m + 0{,}7\theta_D$ is a universal homologous temperature and θ_D is the Debye temperature. The energy of interaction between gold and a vacancy in iridium, $(E_{VacAu})_{Ir} = -26$ kJ/mole, correlated with known charge dependencies of such interaction energies for the volume diffusion of intrinsic-series impurities in single crystals of tungsten and gold.

When the mono-Ir samples were annealed in TGV, they were loaded with impurities forming vacancy-impurity complexes (VICs). Under these conditions, the diffusion of substitutional atomic probes (including gold) was determined not by equilibrium vacancies, but by "impurity" vacancies, which appeared thanks to thermal dissociation of VICs. The binding energy of VIC pairs in mono-Ir: $(E_{VIC})_{Ir} = -(116 \pm 16)$ kJ/mole correlated with a linear dependence of E_{VIC} on the melting temperature of transition and noble metals doped with carbon and hydrogen.

Diffusion and Conformation Relaxation Control of Charge Compensating Ion Transport in Electrodeposited Polymers

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Changes in the oxidation states of the electrodeposited polymers are accompanied by the flow of the charge compensating ions in and out of the polymer network. This phenomenon is controlled by the diffusion as well as the relaxation of the structure of the polymeric chains. While the former follows a Cottrell behavior under a chronoamperometric (CA) regime, the latter effect appears as a point of maximum in the CA curves with the relaxation time corresponding to the maximum current follows:
$t=t_0\exp((\Delta H+Z_c\eta)/RT)$
Where η is the overpotential required to open(close) the network to ions, Z_c the charge required and ΔH is the chemical energetic of the process with field off.
In this work the electrodeposited polymeric films based on aniline (AN),o-toluidine (OT), N-methylaniline (NMA) and co-polymers of (AN-OT) and (OT-NMA) were studied in both acidic aqueous and acetonitrile/$LiClO_4$ solutions in the temperature range of 278-323K.
In aqueous solutions it was not possible to submit the films to cathodic potentials less than -700mV prior to the oxidative CA runs due to the interference of H_2 evolution and diffusion was the sole mechanism of the ions transfer. Diffusion coefficients in the range of 10^{-13} to $10^{-11}cm^2s^{-1}$ for the highly packed and large anions to the least packed and small anions was obtained with the additional finding of the fractal nature of the structure as witnessed by different scaling lengths of different anions. In non-aqueous medium the cathodic potential up to -1900mV were applied to the film prior to CA runs and points of maxima in the CA's were observed. Z_c in the range of 2000-9500 $Cmol^{-1}$and ΔH of 10-30 $kJmol^{-1}$for the least to the most compact structure were obtained.

Diffusion of Nb in Nb-H Alloys

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Diffusion in metals is generally suppressed under hydrostatic pressure. It was, however, found that interdiffusion in the Cu-Ni system was remarkably enhanced under 5 GPa H_2 because a great quantity of vacancies were induced in the system. In the Cu-Ni system, elevated hydrogen pressure is necessary to dissolve a large amount of hydrogen in the solid phase. However, hydrogen solubility in Nb is quite large even under 0.1 MPa H_2 (i.e. the atomic ratio $H/Nb \approx 0.45$ at about 400K).

In the present work, the tracer diffusion coefficients of ^{95}Nb, D_{Nb}, in NbH_x alloys ($x = 0.05 - 0.34$) around 0.1 MPa H_2 in the temperature range from 823 to 1323 K have been determined by means of an ion-beam serial sputter-microsectioning technique. The logarithm of D_{Nb} in the NbH_x alloys increases linearly with increase of hydrogen solubility, x, up to 0.1, suggesting that the concentration of vacancies which enhance the diffusion is proportional to the hydrogen solubility in the alloys. As a result, the diffusion coefficient of ^{95}Nb increases by about 10, 100 and 10^7 times in the $\mathrm{NbH}_{0.05}$, $\mathrm{NbH}_{0.1}$ and $\mathrm{NbH}_{0.34}$ alloys, respectively.

Advanced Diffusion Studies with Isotopically Controlled Semiconductors

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Semiconductor heterostructures which consist of layers of isotopically enriched material sandwiched between layers of natural composition are highly suitable for studying self-diffusion, the fundamental process of matter transport in solids. Utilizing a multilayer structure with alternating natural and isotopically enriched layers the self-diffusion at multiple interfaces located at various distances from the surface provide direct information about the distribution of the native point defects mediating self-diffusion. In the case when the thermal equilibrium concentration of the native defects is established, a homogeneous broadening of all natural/isotope interfaces is expected. However, in the case when the native defect concentration deviates from thermal equilibrium, e.g. as a consequence of dopant diffusion or radiation effects, the broadening of the isotope structures reflects the distribution of native point defects which is established under the particular experimental condition.

Diffusion studies with isotopically enriched Si and Ge isotope multilayer structures and isotopically controlled Ga-based III-V compound semiconductors are presented in this contribution. The structures were grown by chemical vapor phase epitaxy and/or molecular beam epitaxy and were analyzed with secondary ion mass spectrometry before and after diffusion annealing. Special attention is paid to the impact of dopant diffusion and proton radiation on self-diffusion in the isotope structures and the modeling of these experiments. It is demonstrated that the simultaneous diffusion of self- and dopant atoms provides information about the mechanisms of self- and dopant diffusion which are not accessible by self- and dopant diffusion experiments performed separately. Moreover, experiments on radiation enhanced self-diffusion with isotope multilayers can be used to determine the migration enthalpy of the native defect mediating self-diffusion.

TARGISOL: Release Measurements for the Optimization of Radioactive Ion Beams

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Very intense beams (up to several 10^{12} ions per s) of radioactive isotopes can be produced with the ISOL (isotope separation on-line) method: a primary beam (protons, neutrons, heavy ions, etc.) induces nuclear reactions in a target. The produced radionuclides are stopped in the target (or in a following catcher). By heating the latter to sufficiently high temperatures, the radionuclides can diffuse out and effuse eventually through a transfer line to the ion source where they are ionized.

Since exotic nuclides are only produced in limited amounts, they are very “valuable”. The release has to be as efficient as possible, i.e. the radionuclides must reach the ion source, be ionized, accelerated and mass-separated before they decay. The release speed is governed by diffusion in the target, the random walk effusion and the adsorption/desorption cycles at each surface collision. The EU-RTD project TARGISOL (HPRI-CT-2001-50033) aims at optimizing ISOL targets in a systematic way: the release from different possible target-and-ion-source units is simulated by a Monte Carlo model, which can predict the release speed for various elements in dependence of the geometry and the used materials.

For potential target matrices where no literature data of diffusion coefficients for the elements in question exist, we determine them by isochronal annealing of activated or radiotracer-implanted samples. This was used e.g. to study the Mn release from various high-melting Cr, Fe and Ni compounds: Cr, CrB_2, CrC_x, Cr_2O_3, CrS, Fe, Fe_2O_3, Ni and NiO.

These off-line studies are complemented by on-line measurements of the release time profile of stable or radioactive tracer isotopes from a complete target-and-ion-source unit. Thus we measured e.g. the diffusion of Sn in graphite, LaC_x, ZrO_2, CeO_x, HfO_2, Ta_2O_5 and CeS.

Results of recent off- and on-line measurements will be presented and future needs for diffusion data will be discussed.

Nucleation and Growth of Product Phase at Reactive Diffusion

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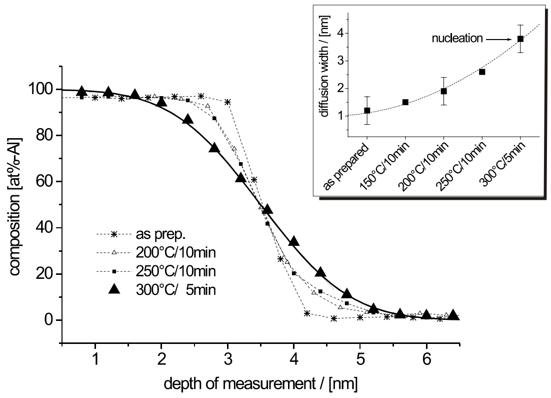
With the actual interest in nano-technology the earliest stages of reactive diffusion get increasingly important. Only a few experimental techniques are able to observe atomic transport on the required length scale. In our experiments we used atom probe tomography, which is a unique tool owing to its 3D analysis with an accuracy of a few Ångstroem.

For the presented study, thin film reaction couples Al/Co were deposited by ion beam sputtering onto tungsten substrate tips of 20 to 50 nm curvature radius. After suitable heat treatments, it is clearly shown that a significant volume diffusion of both reactants precedes the formation of the first product Al_9Co_2. However, at maximum the interdiffusion length is found to be 3.5nm, which allows quantifying the critical composition gradient for nucleation to be 0.3 nm^{-1}.

The product phase appears in a globular morphology. The earliest Al_9Co_2 particles quickly grow to a diameter up to 10 nm before a dense product layer is formed. This fast growth is only understood by interfacial transport. By the comparison with a kinetic model adapted to this special situation, reaction constants at the interfaces are estimated, which are hard to determine otherwise. For the overall reaction, the model predicts non-integer kinetic exponents in the range of 2 to 3, i.e. the reaction is much faster than in the case of ordinary parabolic or linear growth.



A Diffusion Model for Chemical Compounds Layer Growth in Multiphase Binary Systems

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We present an up-graded model and an appropriate software for reaction diffusion in multiphase binary systems. It is based on consideration of unilateral diffusion and allows to consistently describe: (i) evolution of diffusion zone structure at realization of various boundary conditions with any number of individual phases on the phase diagram and reagent diffusion coefficients, which may differ radically in various phases; (ii) development of the process starting with any diffusion couple, including an initial elemental couple at supplying in-diffusing component from solid, liquid or gaseous phases; (iii) behaviour of very thin layers with practically stoichiometric composition, starting with the moment of their appearance and including the possibility of their disappearance and repeat appearance caused by a change in process conditions. Computation of diffusion processes is accompanied by their complete visualization. Minimum thickness of a diffusion layer described in this model is essentially not limited and determined by single spatial step of calculation grid. This makes it possible to track the behaviour of very thin and hardly observable layers in the diffusion zone, the presence or complete absence of which is currently most debatable.

On the basis of reaction diffusion model aforementioned calculations on formation and growth laws of diffusion layers were carried out for a number of silicide and carbide systems containing phases, which usually are hardly observable in the diffusion zone. Calculations involving various diffusion couples along with corresponding experimental data provide complete and reliable information about all layers, regardless the absolute value of their growth rate.

Fractal Self-Assembled Nanostructures on Monocrystalline Silicon Surface

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We present ultra-shallow (5-30 nm) diffusion profiles heavily doped with boron that are performed from the gas phase using controlled surface injection of self-interstitials and vacancies into n-type Si(100) wafers. The diffusion profiles of this art are found to consist of both self-assembled silicon quantum wells and wires formed naturally between the δ - barriers and spikes heavily doped with boron.

The parameters varied in the course of experiment were the diffusion temperature (800°C-1100°C), the Cl levels in the gas phase as well as the thickness of the oxide overlayer formed previously on both the working and backside of the Si(100)-wafer. The diffusion profiles were studied using the SIMS, CV, cyclotron resonance (CR) and scanning tunneling microscopy (STM) techniques appeared to exhibit strong deformed potential fluctuations (DPF) induced by the self-interstitials microdefects that are created around the P_b centers at the $Si\text{-}SiO_2$ interface. The DPF that enhance the diffusion of boron respectively along the [111] and [100] crystallographic axis caused by the kick-out (1100°C) and vacancy related (800°C) diffusion mechanisms result in the formation of fractal distribution of the δ - barriers and spikes heavily doped with boron.

The CR angular dependencies are evidence of the system of the longitudinal and lateral self-assembled silicon quantum wells and wires, which are created between the δ - barriers and spikes that exhibit ferroelectric properties due to the negative-U self-compensation of the centers of boron, $2B^0 \rightarrow B^+ + B^-$.

Self-diffusion in Nickel-manganese Alloys

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Alloys of the nickel-manganese (Ni-Mn) system have recently attracted interest due to its anti-ferromagnetic properties and potential applications in the magnetic storage industry. Furthermore according to the phase diagram of this system there are three single-phase areas with different lattice structures present in equiatomic $Ni_{50}Mn_{50}$ at different temperatures. Diffusion studies in this intermetallic compound can directly show the influence of phase transitions on the diffusivity at the same composition.

Self-diffusion of nickel and manganese has been investigated in $Ni_{50}Mn_{50}$ alloys over wide temperature ranges. The alloys were prepared at the University of Wisconsin. The diffusion of ^{63}Ni and ^{54}Mn was measured by the radiotracer method at the University of Münster. Experiments were performed on disordered fcc, B2 and $L1_0$ structure regions present in this compound.

The diffusivity of manganese was found to be significantly faster (factor 3 to 5) than the nickel diffusivity in all single phase structures. More than one order of magnitude diffusivity increase was observed upon the fcc – B2 transition. The activation enthalpy of nickel self-diffusion in the disordered fcc phase higher than the corresponding value for manganese. In the B2 phase there is only a slight difference between the activation enthalpies of the components which lies within the error bars. A comparison of the present experimental data on tracer self-diffusion with literature data on interdiffusion in the Ni-Mn system shows good agreement between experimental interdiffusion coefficients and those deduced by using the Darken-Manning equation and the present tracer diffusion coefficients. The thermodynamic factor was found to vary from 3 to 4 depending on the structure.

Diffusion in Decagonal and Icosahedral Quasicrystals and a Hexagonal Approximant

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We present our investigations of gallium diffusion in decagonal AlNiCo quasicrystals in both principal directions and of gallium diffusion in icosahedral AlPdMn quasicrystals. Gallium tracer is isoelectronic to aluminium. Aluminium self-diffusion cannot be measured using conventional tracer techniques. The depth-profiles of the isotopes ^{69}Ga and ^{71}Ga were analyzed by SIMS profiling at the University of Darmstadt. We compare our results in decagonal AlNiCo with experimental data on self-diffusion of cobalt and nickel and with MD-simulations of Al self-diffusion from literature. Our experiments and the MD simulations show that the diffusion parallel to the decagonal axis is faster than perpendicular to it.
In addition we carried out diffusion studies of the major component zinc in icosahedral ZnMgY, icosahedral ZnMgHo and a hexagonal ZnMgY approximant along both principal directions. We report the Arrhenius parameters and compare the diffusion behaviour of the various materials.

Diffusion in Bulk-metallic Glass-forming Pd-Cu-Ni-P Alloys from the Glass to the Equilibrium Melt

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Since the discovery of bulk metallic glasses there has been considerable reseach effort on these alloys. Now the undercooled melt between melting temperature and caloric glass transition temperature, which has not been accesible before due to the rapid onset of crystallisation, can be investigated and recent theories can be tested [1]. We report on radiotracer diffusion measurements in metallic bulk-glass-forming Pd-Cu-Ni-P alloys. Serial sectioning was performed by grinding and ion-beam sputtering. The time, temperature as well as the mass dependence, expressed in terms of the isotope effect E, of Co-diffusion were investigated [2,3]. In the glassy state as well as in the deeply supercooled state below the critical temperature T_c, where the mode coupling theory predicts a freezing-in of liquid-like motion, the measured very small isotope effects indicate a highly collective hopping mechanism involving of the order of ten atoms. Below T_c the temperature dependence shows Arrhenius-type behavior with an effective activation enthalpy of 3.2 eV. Above T_c the onset of liquid-like motion is evidenced by a gradual drop of the effective activation energy, resulting from the decay of hopping barriers, and by the validity of the Stokes-Einstein equation, which is found to break down below T_c. This strongly supports the mode coupling scenario. The Stokes Einstein equation is presently tested for other constituents of the alloy. Co-isotope effect measurements, which have never been carried out near T_c in any material, show atomic transport up to the equilibrium melt to be far away from the hydrodynamic regime of uncorrelated binary collisions.

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Simulation of Diffusion Kinetics in Intermetallic Compounds of $D0_3$ and $L1_2$ Structures

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Diffusion in ordered intermetallics involves often a competition of several basic mechanisms. Indeed, mass transport mediated by monovacancies is energetically unfavorable due to the creation of anti-site defects either permanently or temporarily, as a part of an order-restoring jump cycle. Recently several alternative mechanisms specific for intermetallics have been proposed. These mechanisms consider the diffusion mediated by divacancy-type complexes (either a divacancy or a triple defect), where the low concentration of divacancy-type defects is compensated by their relatively high mobility. However, the presence of several mechanisms of atomic jumps makes analytical estimates of self diffusion coefficients practically impossible.

In this work the diffusion mechanisms mediated by vacancies and divacancy-type defects in ordered alloys with $L1_2$ and $D0_3$ structure are studied by lattice kinetic Monte-Carlo method. The energies of vacancies and divacancy complexes in different sublattices, as well as the migration barriers are estimated by molecular statics relaxation using embedded-atom potentials for the systems Ni_3Al and Fe_3Al. The obtained energy values define the relative rates of individual jumps, which constitute the input for Monte-Carlo simulations. The simulations are performed in a crystal composed from several tens thousands of atoms, containing either a vacancy or a pair of vacancies, with different initial configurations. The trajectories of diffusing defects are analyzed in order to estimate the relative frequencies of possible diffusion patterns and partial self-diffusion coefficients of different kinds of atoms in the studied alloys.

Activation Volume for Interdiffusion in B2 Type Intermetallic Compounds NiAl and FeAl

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Activation volume for interdiffusion, $\Delta\widetilde{V}$, in B2 type intermetallic compounds NiAl (40 ~ 49 at%Al) and FeAl (40 ~ 50 at%Al) has been obtained above 0.75 T_s (T_s: solidus temperature) by measuring the interdiffusion coefficient under the pressure from 0.1 MPa to 5 GPa. $\Delta\widetilde{V}$ in NiAl shows almost constant value of 1.0 V_0 (V_0: molar volume of alloys), suggesting that the divacancy mechanism is dominant at higher temperature region. On the other hand, $\Delta\widetilde{V}$ in off-stoichiometric FeAl increases from 0.6 to 0.8 with increasing temperature, showing that the contribution of divacancies to diffusion increases with increasing temperature. Di-ffuion mechanisms in NiAl and FeAl have been discussed with the help of our experimental data on intrinsic diffusion in them.

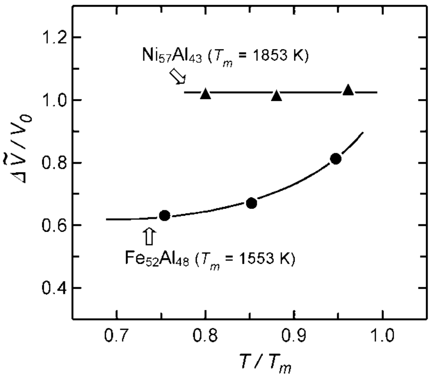

Fig. Temperature dependence of $\Delta\widetilde{V} / V_0$ in $Ni_{57}Al_{43}$ and $Fe_{52}Al_{48}$.

Dynamics of Water in Hydrous Aluminosilicate Glasses Studied by Quasielastic Neutron Scattering

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We studied the dynamics of water in $NaAlSi_3O_8$ and $Ca_{0.5}AlSi_3O_8$ glasses with a water content of up to 8 wt-% using quasielastic neutron scattering. IR spectroscopic measurements show that for water contents up to 3 wt-% it exists mainly as OH groups in these glasses and that for higher water contents predominantly H_2O molecules are formed. In the neutron scattering experiments we used a backscattering spectrometer (IN10, ILL Grenoble) as well as a time-of-flight spectrometer (IN6, ILL Grenoble) to investigate dynamics in the time window from 0.2 ps to 2 ns. We measured both elastic scans and inelastic spectra in the temperature range from 2 K to 420 K. The elastic scans show that the dynamical processes in the Ca glass with 8 wt-% water set in at lower temperatures (≈120 K) than in the corresponding Na glass (≈150 K). This is corroborated by the broadening of the inelastic spectra. The shape of the scattering function indicates a distribution of activation barriers for the dynamics of the water due to the disordered structure of the glasses. In the Ca glass the average activation energy (0.16 eV) is smaller than in the Na glass (0.27 eV) and the (normal) distribution of activation barriers is narrower in the Ca glass ($\sigma = 0.07$ eV) than in the Na glass ($\sigma = 0.11$ eV). The dynamical process may be identified with rotational motion of the water molecules. This is faster in the Ca glass though the long-range translational motion is slower.

Mixed-Alkali Effect in Sodium-rubidium Borate Glasses

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A series of $0.2[X\mathrm{Na_2O}\cdot(1\text{-}X)\mathrm{Rb_2O}]\cdot0.8\mathrm{B_2O_3}$ ion conducting glasses have been investigated as functions of composition (X = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) and temperature (T = 504-654 K) by means of impedance spectroscopy and tracer diffusion technique. The activation enthalpies and pre-exponential factors of the Arrhenius-type temperature dependent dc conductivities and ^{22}Na and ^{86}Rb diffusivities are determined. Whereas, the dc conductivity reveals the sum of contributions of both ionic species in the mixed-alkali glasses the tracer diffusion is element selective. From these complementary experiments we expect better insight into the ion dynamics of mixed-alkali glasses and the mixed-alkali effect (MAE). The following features of the MAE were observed as a function of relative alkali content X: i) a minimum in glass-transition temperature near $X = 0.2$, ii) a minimum in conductivity near $X = 0.4$, iii) a corresponding maximum in activation enthalpy of conductivity near $X = 0.4$, iv) a diffusivity-crossover of ^{22}Na and ^{86}Rb diffusivities near $X = 0.2$ in the investigated temperature range. In contrast to ^{22}Na, the ^{86}Rb diffusivity at constant temperature has a nearly exponential X dependence in the whole composition range. This points to a major difference in diffusion of the smaller Na and the larger Rb ions. The charge- and tracer-transport are found to be different which is expressed by a Haven ratio smaller than unity.

Modeling and Numerical Simulation of Diffusion Processes during Non-Protective Oxidation and Internal Corrosion of Ni-base Alloys

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The aim of this study is the prediction of internal corrosion attack as a consequence of non-protective oxide scale formation. Even though modern high-temperature alloys are designed in such a way that they are able to form a dense and adherent alumina scale repeated spalling and cracking due to high mechanical and thermal loads may result in a local depletion of Al and eventually in a transition to internal oxidation and nitridation. This kind of deep internal corrosion, which was experimentally studied, e.g., on wedge-shaped specimens of the single-crystalline Ni-base superalloy CMSX-4, gives rise to a deep embrittlement of the surface layer and, therefore, a substantial reduction in service life.

Since the progress of the internal corrosion process is determined by diffusion and chemical reaction of the corrosive species and the corresponding alloying elements, i.e. O, N, Ti and Al, the damage scenario mentioned above has been modelled by a combination of a finite-element tool to solve the diffusion differential equations numerically and the powerful thermodynamic software ChemApp. The rate of oxide spalling/cracking was estimated by means of COSP (cyclic oxidation spalling programme) taking the experimental results into account. This procedure allows the calculation of the concentration profiles of all the species participating in the corrosion process and the prediction of critical conditions, when the local Al content drops below the minimum concentration required for superficial scale formation and non-protective breakaway accompanied by internal corrosion starts to occur.

Defects-diffusion-stress Relationships in Modeling of the Oxidation and Degradation Processes of Alumina Formers

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The modeling of the oxidation and degradation processes of the best metallic materials, being the so-called alumina formers, was elucidated in terms of the matter transport via grain boundaries of α-Al_2O_3. This paper indicates that such an approach needs to be re-visited. It is indicated that the following factors should be taken into account in modeling : (i) diffusion via point defects in the unstable alumina polymorphs (γ, δ, θ) which grow during the early oxidation stages; (ii) outward growth of the whisker-type oxide from the dislocation pipes in oxide grains; (iii) formation of the oxide in three-dimensional defects, being the cracks in the oxide layer; (iv) stress-induced outward oxide growth resulting from the formation of the new oxide within the existing layer.

The mentioned above effects are illustrated and discussed for the oxidized FeCrAl-type alloys and β-NiAl intermetallic compound a variety of experimental methods being applied, such as : two-stage-oxidation, SIMS, SEM.

It is shown that basing on the modified approach better and self-consistent models of the oxidation and degradation mechanisms of alumina formers can be proposed.

Experimental Errors in Studying the Defect Mobility in Nonstoichiometric Metal Oxides

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Important information on the mobility of predominant defects in transition metal oxides may be obtained in studying the kinetics of nonstoichiometry changes as a function of temperature and oxidant activity using modern microthermogravimetric techniques. One of the most important methods enabling the determination of chemical diffusion coefficient in these compounds is so-called re-equilibration kinetic method. As the chemical diffusion is a process of ambipolar migration of defects under their concentration gradient, the chemical diffusion coefficient in nonstoichiometric compounds can be determined from mass changes of a given sample when going from one equilibrium state to another. If no hysteresis is observed in oxidation and reduction runs, it may be considered that the rate determined step is the ambipolar diffusion of defects. The main goal of the present paper is an attempt to show that several systematic errors in such experiments may lead to erroneous results. First of all, geometry of the sample should be rationally chosen in order to eliminate the influence of corner effect on re-equilibration kinetics. However, one of the most important systematic errors may originate from carrier gasses used to obtain the necessary oxygen partial pressure. If only one carrier gas is used – as usually – the Archimedes effect is to be expected when the oxygen partial pressure is changed. This source of systematic errors may be eliminated by using two carrier gases (Ar and He), in which the Ar/He ratio is chosen in such a way that the density of this gas mixture is exactly the same as that of oxygen. Another systematic error may result from insufficient supply of the oxidizing gas to the surface of re-equilibrated sample. All these problems are illustrated by the results obtained on nonstoichiometric nickel and cobalt oxides.

Diffusion in Anionic Conducting Oxides under Non Equilibrium Conditions

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This paper concerns the transport processes which occur in anionic conducting oxides subjected to a chemical potential gradient or an applied electrical field, at high temperature. The general equations allowing to describe the transport processes in the anionic and cationic sublattices are given. Experimental and calculated kinetic demixing results obtained with yttria-doped zirconia are reported. They show the importance of the kinetic demixing reactions in the cationic sublattice, which are more or less important depending of the boundary conditions but which concern always the near surface region of the considered materials. They have then an important influence on both the oxide reactivity and the material deterioration in practical situations. On the other hand, an experimental procedure for the determination of the oxygen diffusion coefficient in ionic and semiconducting oxides is described. Experimental results obtained with yttria-stabilized zirconia are reported. They show the advantages of this procedure and the complementary information obtained by the analysis of these results and those of self-diffusion and ionic conductivity.

Thermo Mechanical Treatment of Nickel and Titanium Aluminides

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Polycrystalline Ni_3Al and TiAl are attractive materials for high temperature structural applications due to their stability in oxidizing and sulphidizing environment up to 700 ^{0}C. They possess significantly higher specific stiffness and similar specific strength than super alloys. Hence, these materials can replace super alloys for high temperature applications (~900^{o}C). TiAl has lower density and can be used for reduction of the component weight up to 50%. Thus, this compound is suitable for aerospace and automobile (high performance vehicles) industries. The major difficulty to include Ni_3Al in engineering applications is its extremely low ductility and inter-granular fracture at ambient temperatures. TiAl, apart from the mentioned brittleness, also suffers from high temperature corrosion. However, the brittleness of these aluminides can be reduced by micro-alloy.

This paper deals with the recrystallization studies on nickel aluminides, deformed to different degrees by rolling. The average grain size dependence with the % elongation is evaluated in the grain size range of 10-35micron. For the nickel aluminide deformed by 50% by rolling, the variation of resistivity and hardness with annealing time is determined.

The homogenized TiAl samples were cold worked and annealed at 1000 ^{0} C. Since the aluminide suffers from low ductility at room temperature, an arbitrary parameter, electrical resistivity, was chosen. Corresponding hardness values were also obtained. Finally a qualitative determination of ductility was made by studying the flow behavior of the alloy around the hardness indentation. Thus a correlation was developed between resistivity, hardness and ductility values. It was then to some extent possible to investigate the TMT cycles on the microstructure and hence on the ductility of the TiAl without going for the actual tensile tests.

Self-Diffusion of Iron in Nanocrystalline $Fe_{64}N_{26}Zr_{10}$ Measured with Nuclear Resonance Reflectivity

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Mössbauer spectroscopy and nuclear resonance forward scattering (NFS) of synchrotron radiation (SR) are well established techniques for studying atomic diffusion in solids. NFS of SR relies on the time domain measurement of the scattered intensity and the information about the diffusive motion is obtained through the modulation of the time dependence of the intensity of the resonantly scattered radiation. In both the frequency domain as well as time domain measurements, the intensity of the Mössbauer radiation gets modified significantly only when the time range of the diffusive motion is comparable to the life time of the nuclear excited state participating in the resonance scattering. This puts limits on the range of diffusivity which can be measured using this technique. In case of ^{57}Fe nuclear resonance, typical diffusivities which can be measured lie in the range 10^{-12} to 10^{-13} m^2/s. In the present work, for the first time, we demonstrate the possibility of using nuclear resonance scattering (NRS) from isotopic multilayers for studying self-diffusion of Mössbauer isotopes over a range several orders of magnitude larger than that accessible through the above techniques. At the same time, the technique is sensitive enough to measure diffusion lengths as small as 0.1nm, which is more than an order of magnitude larger than the sensitivity of depth profiling techniques like SIMS, AES.

Nanocrystalline $Fe_{64}N_{26}Zr_{10}/^{57}Fe_{64}N_{26}Zr_{10}$ isotopic multilayer have been prepared by magnetron sputtering. Diffusivity in these multilayers have been studied at ID22N beamline of ESRF using NRS. The measured values of activation energy and the pre-factor are 0.8 ± 0.1 eV and $\log D_0 = \exp -12 \pm 2 m^2 s^{-1}$, respectively. As compared with amorphous FeN[1], the activation energy for self-diffusion of Fe in the present system is significantly lower than that in the amorphous FeN of similar composition.

[1]. M. Gupta et al Phys. Rev. B**65** (2002) 214204.

Impedance Spectroscopy Analysis of Li Ion Dynamics in Single Crystal, Microcrystalline, Nanocrystalline, and Amorphous $LiNbO_3$

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Impedance spectroscopy was employed to investigate the Li ion diffusivity in single crystal, microcrystalline, nanocrystalline and amorphous $LiNbO_3$. Nanocrystalline $LiNbO_3$ with average grain sizes ranging from 15 nm to 100 nm was prepared by high-energy ball milling from the microcrystalline starting material. The amorphous form was prepared by a double alkoxide (sol-gel) route.

The frequency dependent conductivity and dielectric constants were measured under oxygen atmosphere at frequencies, $\omega/2\pi$, from 5 Hz to 13 MHz and at temperatures from 300 K up to at most 450 K in the case of the nanocrystalline and amorphous samples, and up to higher temperatures in the case of the single crystal and microcrystalline material. The ionic conductivity at, e.g., 450 K was found to increase by about 7 orders of magnitude in going from the single crystal through the microcrystalline to the corresponding nanocrystalline and amorphous forms. The increased free volume in the amorphous material could be responsible for the enhanced conductivity, while in nanocrystalline $LiNbO_3$ the behaviour is governed by the increased fraction of the interfacial regions which are highly disordered and may in the present case be visualized as amorphous. In all cases the real part of the conductivity can be represented by the power law $\sigma' = \sigma_{dc} + A\omega^s$, with $0.55 < s < 0.77$, and can be scaled to give master curves. Impedance data were also analyzed in the complex plane plot (with ω as implicit parameter) in a trial to separate the bulk conductivity from the grain boundary and electrode effects. Both the dc conductivity and the frequency corresponding to the apex of the impedance arc, i.e. the relaxation frequency $\omega_r/2\pi$, were found to follow Arrhenius behaviour with similar activation energies. The dielectric constant values calculated at $\omega_r/2\pi$ increase with decreasing grain size and vary only little with temperature.

Inverse T-sample Method of Determination the Interdiffusion Coefficients in the Cu-Ni-Sn System

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Methodology is presented for solving the inverse diffusion problem in ternary system - determining the interdiffusion coefficients of phases formed in a ternary diffusion couple in T-sample configuration. Method requires only one annealing of the T-sample and makes it possible to calculate the matrix of the diffusion coefficients in the $(CuNi)_6Sn_5$ and $(CuNi)_3Sn$ ternary intermediate phases under low temperature. The concentration profiles and electron micrograph of the diffusion zone was obtained in the ternary Cu-Ni-Sn system annealed for 64 hours at 180°C. Numerical solution of the diffusion problem for two-dimension sample was obtained using concentration dependent intrinsic diffusion coefficients in the intermediate phases. After this calculation we compare the experimental and calculated morphology of the diffusion zone, determine the differences between concentration profiles and locations of the interphase boundaries. We use the genetic algorithm for minimization of this differences and, therefore for the determination of the concentration dependent intrinsic diffusion coefficients and the matrices of the mutual diffusion coefficients in compounds.

Phase competition in this ternary system with special configuration of T-sample leads to lateral diffusion of Cu, formation $(CuNi)_6Sn_5$ compound between Ni-Sn side and suppression of other Ni_xSn_y intermediate phases.

Kinetics of Zero Flux Planes in Ni-Cu-Zn

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Zero Flux Planes (ZFP) occur commonly in ternary and higher-order multicomponent alloys. ZFP's for a component manifest as stationary or symetrically moving planes disposed about the Matano interface. In contrast to the normal global mixing that occurs in a binary diffusion couple, the presence of a stationary ZFP requires that mixing of the blocked component occurs unilaterally through the release of pairs of coupled depletion-repletion waves that increase the average concentration in the component-poor alloy, but decrease it in the component-rich alloy. We previously analyzed the kinetics of multicomponent diffusion near ZFP's for single-phase couples based on Cr-10at%, Al-10at%, Ni-80at% with a series of alloys having a concentration difference vector with a magnitude of 1at%. It was demonstrated that the spreading rates of the ternary diffusion zones could be reduced by choosing the composition vector's orientation in composition space to be near the Euler angle for the minor eigenvector in the diffusivity matrix. Moreover, a critical angle $\psi^* \approx -29^{\circ}$ was found in Cr-Al-Ni alloys, which exhibit minimal total rates of interdiffusion with composition vectors selected within $\psi^* \pm 5^{\circ}$. The reduced atomic transport was associated with the proximity of the orientation angle, ψ^*, to that for the ZFP for the *major* component. Similar analyses on ternary couples based on Ni-43.5at%, Zn-25at%, Cu-31.5at% show that diffusive spreading is reduced for couples located in composition space close to the ZFP of the *minor* component.

Influence of Platinum and Palladium on Diffusion in beta-NiAl Phase

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A new method for calculating composition-dependent interdiffusion coefficients in ternary systems [1] has been applied to diffusion couples in the beta-(Ni, Pt)Al and beta-(Ni, Pd)Al systems.

Results show in particular that the direct coefficient $\tilde{D}^{Ni}_{AlAl}$ is an ascending function of platinum or palladium content. They also reveal a particular behaviour of the cross coefficients $\tilde{D}^{Ni}_{PtAl}$ and $\tilde{D}^{Ni}_{PdAl}$ for an aluminium content of 50at.%.

These results will be discussed in relation with the fact that Pd and Pt substitutes for Ni in the nickel sublattice (according to ab initio calculations) and in relation with proposed diffusion mechanisms in beta-NiAl.

[1] R. Bouchet and R. Mévrel, Acta Materialia 50 (2002), pp 4887-4900.

Diffusion coatings for Corrosion Protection of Structural Materials

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Diffusion coatings were produced using the pack cementation process on Ni-base materials as well as on austenitic and ferritic steels, which proved to enhance the corrosion resistance in reducing sulphidizing atmospheres and under metal dusting conditions. Beside of simple Al-Diffusion coatings advanced codiffusion coatings of the Al-Ti-, Al-Si- and Al-Si-Ti-type as well as two-step Cr-Al diffusion coatings were investigated. Appropriate diffusion powder mixtures were identified by thermodynamical calculations. Especially the codiffusion coatings show a complex phase composition including the formation of different intermetallic phases. Contrary to Ni-base and austenitic alloys the formation of diffusion layers on ferritic steels is irregular. Possible explanations for the different diffusion behaviour depending on the type of substrate alloy are discussed.

Annealing of Fe-15at.%Cr Alloy in N_2-H_2 Gas Mixtures: Effect of Hydrogen

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The effect of hydrogen during annealing of Fe-15at%Cr alloy on the diffusion of nitrogen and chromium, the formation of nitride and the selective oxidation of chromium was investigated. Samples were exposed to an annealing gas mixture with different amounts of hydrogen in an infrared heating furnace and heated to 800°C for 1 minute then cooled down to room temperature. After the experiments, field emission scanning electron microscopy (FE-SEM) equipped with EDX, X-ray photoelectron spectroscopy (XPS) were employed to characterize the morphology, elemental depth profiles and the chemical state of the elements.

Different hydrogen content in annealing atmosphere led to different near-surface properties, i.e. Cr-content, phase composition as well as thickness of the layer. The thickness of the heat-treatment affected zone increased with the increase in the content of hydrogen in the annealing atmosphere, while the chromium to iron ratio in the top layer (Cr/Fe atomic ratio up to 10nm from the top surface) decreased with the increase in the content of hydrogen. In the sample annealed in 100%N_2, the formation of Cr-nitride was observed.

B and N Segregation on Dual Phase Steel after Selective Annealing

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The surface modification of dual phase steel prior to hot dip galvanizing is necessary to improve the wettability of the steel surface by the zinc melt. By changing the water vapour partial pressure in the annealing atmosphere a surface modification by selective oxidation of minor elements is possible. During the investigation of selective oxidation on dual phase steel the formation of BN and B oxides was observed at different dew points. In order to achieve a better understanding of BN formation at a very low dew point (-60°C) and B oxide formation at a higher dew point kinetic investigations were carried on DP 500 alloy. Experiments are performed in 5 % H_2-N_2 atmosphere at two different annealing temperatures, 500 and 800°C, and different times, 15, 60 and 120 s, for kinetics investigation on formation of Chromium nitrides and Boron nitrides as well as Boron oxides. Samples are heated in an infrared furnace and surface morphology and chemistry is investigated by means of FE-SEM equipped with EDX. XPS measurements are used for quantitative elemental depth profiles.

Study of Fe Diffusion in Cr_2O_3 by Secondary Ion Mass Spectrometry

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Cr_2O_3 layers grown by thermal oxidation on stainless steels are effective to protect these alloys against corrosion by oxidation at high temperatures. In order to check if these Cr_2O_3 layers play the role of a diffusion-barrier for Fe from metallic substrates in those alloys, Fe diffusion has been investigated in high density polycrystalline Cr_2O_3, obtained by hot pressing, and in Cr_2O_3 layers grown on Ni-30%Cr alloy. A film of Fe was deposited on the surface of either polished polycrystalline Cr_2O_3 or on the outer surface of the Cr_2O_3 layers on Ni/Cr. Then the iron film was oxidized in pure oxygen at low temperature for short time before diffusion annealing. The diffusion experiments were performed from 720^o C to 1100^o C, under oxygen partial pressure of 10Pa. The Fe diffusion profiles were determined by secondary ion mass spectrometry (SIMS). The experiments led to the determination of Fe effective diffusion coefficients (D_{eff}), determined in the first part of the diffusion profile, using a solution of Fick's second law for diffusion from a thick-film. Le Claire's model was used to determine the product $D_{gb}\delta$ from the tail of the diffusion profiles, where D_{gb} is the grain-boundary diffusion coefficient and δ is the grain-boundary width. Hart's equation allowed to obtain both the bulk and the grain boundary diffusion coefficients. The dependence of these diffusion coefficients on temperature are described by means of Arrhenius' equations. Analysis of the results obtained in polycrystalline Cr_2O_3 and in Cr_2O_3 layers show that the microstructure of the material strongly affects the diffusivity of the iron. Comparison of iron diffusion with chromium self-diffusion in Cr_2O_3 shows that iron diffuses slightly slowly than chromium.

The Effect of Grain-Boundary Diffusion during the Oxidation of Cr-Containing Steels

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Even though the oxidation behavior of steels is generally considered as to be widely understood, a closer look reveals some question marks, e.g. regarding the influence of the substrate grain size on the overall oxidation kinetics.

At temperatures below 570°C the main constituent of the oxide scale formed on top of low alloy steels is magnetite. As shown by gold marker experiments it grows outward and inward at the same time, the latter exhibiting a gradual transition to the more stable spinel compound $FeCr_2O_4$. As indicated by intergranular-oxidation attack below the superficial scale inward scale growth seems to be driven by oxygen transport along the grain boundaries serving as fast diffusion paths. This is supported by thermogravimetric oxidation tests in air on low-Cr steels with varying grain size: The smaller the grains the slower the oxidation rate.

Recently, a numerical model for the diffusive transport processes based on the finite-difference approach has been developed, which distinguishes between fast grain-boundary diffusion and bulk diffusion. Qualitatively, it is capable to predict the relationship between substrate grain size and inward oxide growth kinetics. Together with the powerful thermodynamic tool ChemApp in combination with a data set for the Fe-Cr-O system the mechanism-based simulation of the overall oxidation process of low-Cr steels is possible.

Strains, Mass Transport and Reaction Interactions at the Metal/oxide Interface: Novel Theoretical Investigations on the Oxidation Kinetics

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When the interfaces metal/oxide and oxide/gas are under the presence of an oxidation atmosphere, they develop chemical reactions that imply the transfer of matter. The study of this transfer, which develops in few atomic planes near the interfaces, is essential for understanding the mechanisms governing the growth of the oxide layer. Moreover, the oxide growth, which depends on the way the chemical reaction takes place, generates chemical deformations and produces complex interactions at several scales (e.g. atomic-mesoscopic) that render any theoretical formulation particularly complex.

In our laboratory several theoretical approaches are under development for studying the oxidation of metals, namely:

- At the macroscopic scale, the use of the irreversible thermodynamics theory has lead us to propose a novel formulation for the velocity of the reaction front including the deformation of the system, generated by the reaction, and the reaction and diffusion of matter.
- At the atomic scale, we developed a molecular dynamics code for determine, near the interface metal/oxide; the mechanical deformations, the temperature gradients, the surface energy, etc.

These two approaches will be debated and are intent to be used for the development of a multiscale formulation for the oxidation of metals.

Studies on Electroless Coatings at IIT Roorkee, India

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Since the introduction of Electroless (EL) coating in 1946 by Brenner and Riddle, the process has been the subject of steady growth. It is one of the most elegant methods available for the production of alloy coatings on surface. The technique involves the autocatalytic reduction, at the substrate/solution interface, of cations by EL bath released from suitable chemical reducing agents. EL coating technique is simple one, as can be manifested just by controlling pH and temperature of the coating bath. Such coatings are reported to provide excellent physical and mechanical properties The electroless coatings are being studied at Indian Institute of Technology Roorkee since 1985. The structural behavior of Ni-P coatings for different phosphorus contents has been extensively studied. As a forward step towards composite coatings, Ni-P-C, Ni-P-Al_2O_3, Ni-P-ZrO_2 etc. have been developed by co-deposition techniques. Ag-graphite coatings produced by EL technique exhibits ~5 times higher wear resistance and ~ 2 times better corrosion resistance apart from being a good electrical conductor. The tribological behavior of elctroless Ni-P-X and Ni-P coatings on steel and aluminium substrates in different conditions i.e., as-coated, heat treated at various temperatures at different extents of time with different normal loads, have been studied in terms of dry sliding friction and wear against counter face of case hardened steel. In Ni-P-X nanocoatings (X= ZrO_2-Al_2O_3-Al_3Zr), X has been produced in-situ and are of nano-size particles. Such coating could be done on carbon fibre of 7µ diameter uniformly. Ni-P-Ferrite nano coatings with thickness less than~.1mm thick, is exhibiting about 20db of absorption of microwave in the rage of 12-18 GHz which can be exploited for radar applications. Micro-thickness coatings are paving ways to Nano coatings. Nanocoatings are the coatings in which either the thickness of the coating is in nano level or the second phase, that dispersed in the coat matrix is of nano-size.

Effect of Self-interstitial Diffusion Anisotropy in Electron-irradiated Zirconium. A Cluster Dynamics Modeling

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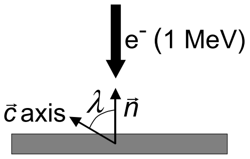
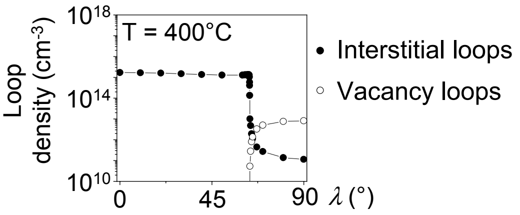
Irradiation of metals leads to the formation of point-defects (vacancies and self-interstitials) that usually agglomerate in the form of dislocations loops. Due to the elastic interaction between self-interstitials and dislocations, the loops absorb in most cases more interstitials than vacancies. That is why the loops observed by transmission electron microscopy are almost always interstitial in nature. Nevertheless, vacancy loops have been observed in zirconium following electron or neutron irradiation [1]. Some authors proposed that this unexpected behavior could be accounted for by self-interstitials diffusion anisotropy [2].

Following the approach proposed by Woo [2], the cluster dynamics model presented in [3] that describes point defect agglomeration was extended to the case where diffusion of interstitials is anisotropic. The model was then applied to the microstructural evolution of a thin foil of zirconium irradiated in a high-voltage microscope. The main result is that, due to anisotropic diffusion of interstitials, the crystalline orientation of the foil has considerable influence on the nature (vacancy or interstitial) of the loops that form during irradiation.





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Phase Transformation and Densification of Nanostructured Alumina: Effect of Seeding and Doping

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In ceramics materials the kinetics of many processes such as phase transformation, sintering, grain growth and creep are controlled by diffusion. In order to produce dense nanostructured alumina from fine gamma alumina powders (< 100 nm), we study the influence of alpha seeding and doping on gamma-alpha phase transformation and densification. Presented results are based on dilatometry measurements, neutron diffraction, SEM, TEM and specific surface areas (nitrogen adsorption, BET model) investigations.

It can be observed that :

- the diffusive phase transformation gamma-alpha involves several processes such as nucleation of alpha phase, rearrangement of gamma crystallites at alpha seed and grain surfaces, formation of porous colonies of alpha alumina bricks with similar orientations.
- The size of colonies depends on the nucleation site density (alpha seeds).
- The pseudo-solubility of doping elements in gamma alumina can be considered to be larger than the solubility in alpha alumina, so doping elements have to be rejected at interfaces and grain boundaries during the phase transformation process.
- Doping elements seem to have no influence on nucleation rate but could modify the redistribution rate of the ions during the transformation by short range diffusion of doping elements.

Kinetics of Precipitation: Comparison between Monte Carlo Simulations and the Classical Laws.

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We test the main approximations and results of the classical laws for nucleation, growth and coarsening by comparison with atomistic simulations of the kinetics of precipitation controlled by solute diffusion.

We investigate the kinetics of phase separation of a solid solution of atom B in a bcc matrix of atom A. Classically, the kinetics is represented by the time evolution the total number of particles and their mean radius. In this work, the kinetics is predicted by two types of models:

- An atomic scale Kinetic Monte Carlo (KMC) model with residence time algorithm of the vacancy
- The Multipreci model, based on the coupling of the classical laws of nucleation, growth and coarsening.

The Multipreci model has been parameterized such that the thermodynamic and kinetic parameters (solubility, diffusion coefficient, interface energy) are identical to that of the KMC.

Under these conditions we find that the classical laws are in very good agreement with the atomistic simulations as long as

- diffusion in the supersaturated solution is dominated by monomer mobility,
- the thermodynamics of the solid solution remains strictly regular.

mportant deviations occur in the incubation period of nucleation when diffusion of n-mers becomes dominant.

Prevention of Kirkendall Voids in Chromised Ni-Plated Austenitic Stainless Steel

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The Cr content of the surface region of stainless steel tubes that are used as superheaters and reheaters in boilers can be enriched to more than 70 mass-% during chromisation. Such layers are susceptible to the formation of sigma (σ) phase while its prevention through the use of chromised Ni-Plated layers is offset by the occurrence of Kirkendall voids. This paper describes how the microstructure of chromised surface protective Ni-Fe layers can be controlled through the optimization of the conditions under which the chromising and post-solution heat treatments are carried out. The Ni-plating and chromising conditions required for the production of layers in which neither σ phase nor Kirkendall void formation takes place are described.

Mechanism and Kinetics of Element and Isotopic Exchange Mediated by a Fluid Phase

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We have developed an analytical model for the fluid-mediated exchange of elements between two crystals that are physically separated from each other. The resulting system of partial differential equations for the element distributions in time and space contain only three non-dimensional parameters for each crystal (β, γ, and δ). A reaction mechanism map can be constructed as a function of γ and δ, the parameter β determines the rate of exchange. The parameters are defined by ratios of thermodynamic, geometric and kinetic properties of the crystals and the fluid that can be estimated or calculated for a given system. For a realistic parameter range it is found that at least six different reaction mechanisms are possible rather than just diffusion or interface control. Some of the more significant observations are that: (1) time scales of equilibration may be substantially greater than the diffusive time scale (x^2/D); (2) rim compositions of zoned crystals may be out of equilibrium with each other and even with the adjacent fluid in some cases and that (3) solubility of the species of interest in the intergranular fluid plays a very important role in determining reaction behavior. The concept of solubility in the intergranular fluid is related to the standard concept of segregation coefficient for grain boundaries.

Model calculations for selected case studies from the literature will be presented at the meeting. Efforts are underway to design experiments on the basis of the model to determine grain boundary diffusion coefficients of elements in an inert matrix and thereby determine indirectly the segregation coefficient.

Evidence for a Diffusion-based Mechanism of Liquid Metal Intergranular Penetration: Case Study of a Ni-Bi Model System

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The aim of this study was to establish the kinetics and the mechanism of intergranular penetration, the phenomenon which is known to occur in some specific systems (Al-Ga, Al-Sn, Cu-Bi, Ni-Bi) above the so-called wetting transition temperature and results in the total replacement of initial grain boundary by a liquid film and two solid-liquid interfaces [1]. This study was done on a model nickel-bismuth system using mainly bicrystals.

Embrittled grain boundaries are described as a succession of three zones : (i) a relatively short micrometer-thick film starting at the liquid/solid interface (length of the order of 100 µm after 16h at 700°C), (ii) a very nanometer-thick film of constant thickness that develops ahead (of the order of the mm) and (iii) a transition zone between the latter and an unaffected grain boundary (of the order of 50 µm).

The thickness of the long thin film was evaluated to be in the range 2-3 nm by Auger electron spectroscopy measurements coupled with a quantification model developed for this purpose [2]. This thickness was confirmed by XPS analysis.

A major implication of these results is that the modelling of intergranular penetration has to be based on a diffusionnal mechanism which operates at a very tip of a nanometer-thick intergranular film, as opposed to models based on a direct SEM observation of a micrometer-thick film.

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Diffusion-Controlled Liquid Bismuth Induced Intergranular Embrittlement of Copper

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The aim of this study was hence to establish the kinetics and the mechanism of bismuth penetration using a copper bicrystal (symmetrical tilt <100> grain boundary with a disorientation angle of 50°) in contact with liquid bismuth at 500°C and in absence of any applied stress.

This contact leads to the intergranular embrittlement of copper. For that reason, grain boundary concentration profiles of bismuth were revealed by room temperature tensile fractures and subsequent Auger electron spectroscopy analysis on fracture surfaces. It has been shown that the maximum level of bismuth is about 1,5 monolayers (near the liquid bismuth / solid copper interface) and that the depth of the brittle zone follows a square root of time dependence.

These results clearly indicate that the contact between this copper bicrystal and liquid bismuth doesn't produce any grain boundary wetting at 500°C and that bismuth grain boundary diffusion is the main limiting phenomenon. Furthermore, a theoretical description of the experimental intergranular concentration profiles is proposed. It is based on the coupling effects between grain boundary diffusion and non-linear segregation in order to explain grain boundary saturation near the interface. As an extension of these conclusions to liquid metal embrittlement phenomenon[1], possible stress effects on the proposed mechanisms are also discussed.

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Annealing of Fe-15at.%Cr Alloy in N_2-H_2 Gas Mixtures: Effect of Hydrogen

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The effect of hydrogen during annealing of Fe-15at%Cr alloy on the diffusion of nitrogen and chromium, the formation of nitride and the selective oxidation of chromium was investigated. Samples were exposed to an annealing gas mixture with different amounts of hydrogen in an infrared heating furnace and heated to 800^{o}C for 1 minute then cooled down to room temperature. After the experiments, field emission scanning electron microscopy (FE-SEM) equipped with EDX, x-ray photoelectron spectroscopy (XPS) were employed to characterize the morphology, elemental depth profiles and the chemical state of the elements.

Different hydrogen content in annealing atmosphere leaded to different near-surface properties, i.e. Cr-content, phase composition as well as thickness of the layer. The thickness of the heat-treatment affected zone increased with the increase in the content of hydrogen in the annealing atmosphere, while the chromium to iron ratio in the top layer (Cr/Fe atomic ratio up to 10nm from the top surface) decreased with the increase in the content of hydrogen. In the sample annealed in 100%N_2, the formation of Cr-nitride was observed.

Lithium Diffusion in $Li_{1-2y}Co_{1+y}VO_4$ for Cathode Materials in Lithium-Ion Cells

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As new cathode materials for lithium-ion batteries, $LiMVO_4$ (M=Ni, Co) with an inverse spinel structure are attractive due to their high voltage behavior. However, these materials suffer from remarkable capacity fading upon several cycles. One of the reasons for such a behavior may be their low chemical diffusion coefficient of lithium ion. It is necessary to clarify the diffusion factors which determine the lithium ion kinetics in materials.
Diffusion coefficient of lithium ion, D_{Li} can be written as $D_{Li} = D_0 \exp(-\Delta G^{\ddagger} / kT)$, where D_0 is the pre-exponential factor, $\Delta G^{\ddagger}$ is activation energy for diffusion, and k is the Boltzmann constant. D_0 is known to be related to cation vacancy concentration. In this study, we have studied variation of D_{Li} in $Li_{1-x}CoVO_4$ with lithium ion removal, x, and $Li_{1-2y}Co_{1+y}VO_4$ with octahedral vacancies introduced by substitution of Co for Li due to thermal reaction have also been investigated to determine the relationship between vacancies and D_{Li}.
Galvanostatic intermittent titration technique (GITT) measurements were carried out to determine D_{Li} in $LiCoVO_4$ and $Li_{0.9}Co_{1.05}VO_4$. Although D_0 values in $Li_{1-x}CoVO_4$ would be increasing due to production of cation vacancies by electrochemical lithium removal reaction, the D_{Li} values in $Li_{1-x}CoVO_4$ was decreasing from about 10^{-10} cm^2 s^{-1} (x=0.05) to 10^{-12} cm^2 s^{-1} (x=0.4), and also decreasing for $Li_{0.9}Co_{1.05}VO_4$. These results indicated that more important factor influenced the lithium diffusion properties. From V and Co *K*-edge EXAFS analysis, the Debye-Waller factors which correspond to the local distortion of each V-O and Co-O bonds were increasing by production of cation vacancy, indicating that the large local distortion of the lattice around V and Co ions occurred. It is suggested that the local distortion effect would cause disturbance for lithium diffusion path. The evaluation of activation energy, $\Delta G^{\ddagger}$ for lithium diffusion path in these materials is necessary, and we should clarify the relationship between local distortion effect and D_{Li}.

Characteristics of Sorption, Solubility and Diffusivity of Hydrogen in Graphite and Novel Carbon Nanostructured Materials, in the Connection with the On-board Storage Problem

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On the basis of the thermodynamic analysis [1-2] of most representative experimental data (for 1998-2002 years) on hydrogen sorption behaviour in graphite and novel carbon-based nanomaterials of *sp*^{2} hybridization (nanotubes, nanofibers, mechanically nanostructured graphite, and others), there have been studied open questions of the nature, capability and reversibility of the hydrogen storage, particularly, for mobile power units. For an interpretation of the thermodynamic and kinetic (diffusion) characteristics obtained in such a way, the recent results (for 2001-2002 years) of 'ab initio' molecular orbital study of adsorption of atomic hydrogen on graphite and carbon nanostructures have been used. Characteristics and nature of five desorption peaks (processes) have been determined and considered, within the technological requirements for electric vehicles. Both experimental and theoretical developments are discussed.

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Grain Boundary Wetting and Pre-Wetting Studied by Grain Boundary Diffusion Measurements in the Cu–Bi System

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Addition of Bi to Cu is well known to provoke grain boundary (GB) embrittlement. At elevated temperatures a thin liquid film covers GBs in the two-phase region (solid+liquid) inducing wetting of GBs. The precise position of the solidus line in this system was recently established. An extended investigation of Bi GB segregation by Auger electron spectroscopy revealed a systematic change in the amount of Bi covering the Cu GBs that indicates a pre-wetting phase transition in the Cu–Bi system (i.e. formation of a liquid-like film at GBs *before* the bulk solidus line is approached).

GB diffusion measurements present a suitable and very sensitive tool for studying structural changes in GBs, especially if a liquid-like GB phase transition occurs. We performed careful measurements of Cu and Bi GB diffusion in a set of Cu–Bi alloys with Bi contents up to 450 ppm. A sudden increase of both, the Cu and Bi GB diffusivities (about two orders of magnitude) was observed at a certain Bi content in the Cu–Bi alloys in the one-phase region clearly *below* the bulk solidus line. The Bi concentration of these steps is the same for self- and solute GB diffusion. It depends on temperature and nearly coincides with the Bi concentration, at which the pre-wetting phase transition was observed by Auger study. As the Bi content is further increased, only a marginal change of the Cu as well as Bi diffusivities is observed. The careful analysis of the diffusion profiles reveals that only a part of the GBs is pre-wetted by Bi.

These experiments manifest unambiguously the pre-wetting GB phase transition in the Cu–Bi system.

Nitrogen self-diffusion in thin film Si_3N_4 isotope heterostructures

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The investigation of self-diffusion in technologically interesting thin film systems based on semiconductors, ceramics, and dielectrics like SiC, Si_3N_4, BN, and Si-C-N raises several analytical problems. The absence of suitable radioactive isotopes for B, N, C, Si prevents the use of the standard radiotracer technique with its high detection sensitivity. Further, the presence of small diffusivities at relatively high temperatures and the dimensions of thin films limited to the μm or nm range require the application of analytical methods with a high depth resolution. An interesting method for the performance of self-diffusion measurements in such systems is the use of stable, isotopically enriched heterostructures, where the tracer is introduced in-situ in the system during synthesis with magnetron sputtering. We present investigations on self-diffusion in polycrystalline and amorphous $Si_3{}^{14}N_4/Si_3{}^{15}N_4/Si_3{}^{14}N_4$ heterostructures with SIMS, NRA, and n-RBS. The self-diffusivities can be described by an Arrhenius law with a single activation enthalpy of $\Delta H = 4.9$ eV and a pre-exponential factor of $D_0 = 1 \times 10^{-6}$ m^2/s in the temperature range between 1200 and 1700 °C. The calculated small entropy of diffusion ($\Delta S \approx 0\text{-}1\ k_B$) indicates a diffusion mechanism with localized point defects, in contrast to smeared out point defects usually found in semiconductors, like Si or Ge. The diffusivities in the amorphous state do not differ significantly from those in the polycrystalline state. The results are compared to diffusivities obtained by a gas-exchange method.

Stress Development and Relaxation During Reaction of a Cobalt Film with a Silicon Substrate

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Stress development and relaxation during reaction of Co films on Si(001) substrates has been studied. Both annealing at a ramp rate of 2°C/min and isothermal annealing at several temperatures have been performed. We performed simultaneously wafer curvature measurements and synchrotron x-ray diffraction. During heat treatment several changes in curvature are observed. From x-ray diffraction, they have been clearly correlated with successive appearing and disappearing of Co silicides : Co_2Si, CoSi and finally $CoSi_2$ below 550°C. Whereas the Co_2Si and CoSi phases relaxed their compressive stress all along the isothermal annealing, no stress relaxation is observed in $CoSi_2$. Modeling of stress buildup thanks to Zhang and d'Heurle model allows one to describe stress development during Co-Si reaction via a reduced number of parameters.

Diffusion in Network Structures

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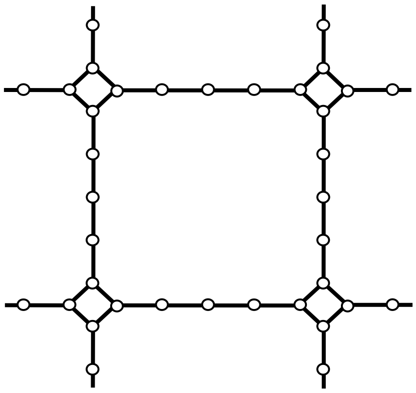
We consider diffusion in structures which are networks of small two or three dimensional atomic clusters connected by one dimensional chains of atoms. This diffusion model can be useful as a model for different diffusion processes: diffusion of alkali ions, diffusion along dislocation networks, grain boundary diffusion etc. Diffusion coefficients and correlation factors for different claster configurations are calculated. Results of theoretical calculations were supported by Monte-Carlo simulation.



Network structure
(example)

Grain Boundary Grooving and Wetting in Metals

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The review is presented on grain boundary grooving and wetting experimental data for model systems with a low solubility in solid state, such as copper – liquid bismuth and aluminum-liquid tin.

The number of liquid grain boundary grooves and channels of different morphological types were found in the experiments. The appearance of the cracks during grain boundary liquid penetration is of special interest.

The thermodynamic conditions for the formation and growth of the grooves and long liquid channels have been formulated for polycrystals.

The kinetic model is presented for grain boundary grooves growth which is based on the two stages mechanism including the stage of solution of solid material and the stage of diffusion through the melt. If the rate of the process is controlled by solution than the grooves deepen as $h \sim t^{1/2}$. In the case of diffusion control the deepening obeys the $t^{1/3}$ law.

The kinetics of grain boundary channels growth under wetting conditions is discussed. It is proposed that the mechanism of the process is based on the grain boundary diffusion. The $h \sim t^{1/2}$ kinetic law is a result of such a solution.

The comparison of the experimental data with the theoretical estimations shows the satisfactory correlation.

Radiotracer Diffusion Measurements of Noble Metal Atoms in Semiconducting Organic Films

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The application of organic field effect transistors (OFETs) for large scale low-cost electronic devices has lead to intense research. Diindenoperylene (DIP) thin films on SiO_2 are a prominent system due to their high structural out-of-plane order. While bottom contact OFET structures can be realized easily, preparation of top contacts might cause diffusion of metal atoms (typically Au) deep into the organic film changing the injection properties at the interface.

For a better understanding of the diffusion of noble metal atoms into crystalline organic films, a radiotracer technique has been used to obtain diffusion profiles for crystalline DIP films.

The first results for Ag show a low concentration of tracer atoms throughout the film, being indicative of a relatively low diffusivity and high surface hold-up, indicative of cluster formation on the surface. Further experiments with crystalline and amorphous DIP and other organic semiconductors are in progress and the results will be discussed with respect to the structural properties of these films.

Long lived transient vacancy distribution in multilayers

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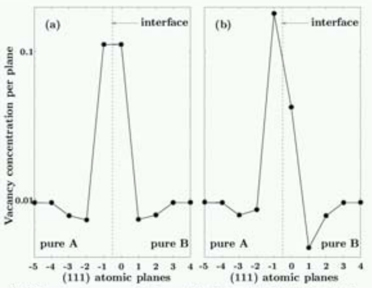
Modeling the vacancy concentration in bi-metallic systems is a key step to understand thermal interdiffusion phenomena. For instance in the kinetics of precipitation, a strong difference between vacancy concentration in the precipitates and in the matrix, may change the precipitate mobility and the coarsening mechanism, the precipitate composition and morphology [1].

The origin of this inhomogeneous vacancy concentration is mainly due to the differences in migration energies ΔE^m and in formation energies ΔE^f of the vacancy in the two phases. The distribution of vacancy sinks and sources or the local lattice deformation should also play an important role.

In this work, we focus on the influence of both ΔE^m and ΔE^f terms on the vacancy concentration profile in a phase separating a multilayer with planar (111) interfaces. The atomic diffusion model is a kinetic Ising-like model with a vacancy exchange mechanism. We perform both kinetic Mean-field and kinetic Monte-Carlo simulations in order to discuss how the vacancy concentration profile (VCP) reaches its steady-state.



KMC vacancy concentration profile (normalized) at $T = 0.258T_c$ for $\Delta E^f = 0$ with (a) $\Delta E^m = 0$ and (b) $\Delta E^m = -0.1eV$

In the figure, we report the quasi-stationary VCP found at the vicinity of an (111) interface for $\Delta E^f = 0$eV. As expected the vacancy strongly segregates into the two interface planes (p=-1,0) because of the tendency of the system to phase separate (the vacancy tends to reduce the number of AB pairs). More surprising is the decrease of the concentration in adjacent planes (p=-3,-2,1,2). This marked decrease, that becomes asymmetric for ΔE^m = -0.1eV (see figure), is rationalized by invoking local correlation effects.

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‘Surfactant-like Dissolution’ of a Thin Deposit for Composition Dependent Diffusion Coefficient

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The dissolution of a few atomic layers thick deposit into a semi-infinite substrate in phase separating systems was investigated recently [1] by computer simulations. It was found that if the substrate atoms have the tendency for surface segregation, there exists a critical temperature (T_k) below which the dissolution takes place layer-by-layer at the deposit-substrate interface but only until the moving interface reaches the subsurface layer. Here the remaining two deposit layers are immersed in the substrate due to the segregation tendency. It is worth noting that the moving interface obeys the *parabolic law*, i.e. shifts proportionally with the square root of the time. Whereas, in case of $T > T_k$, in spite of a relatively thick deposit, the segregation leads to a rapid enrichment of the surface in the substrate atoms and thus to burying of the almost intact deposit film. Then, two simultaneous layer-by-layer dissolution modes take place and compete with each other: from the top and from the bottom of the deposit (surfactant-like dissolution).

In the above calculations the tracer diffusion coefficients were considered composition independent. Here, the influence of the composition dependence of the diffusion coefficient [2] on the surfactant-like dissolution and the time dependence of the interface shift will be shown. In the case of composition dependent diffusion coefficient, the previously observed surfactant-like dissolution mode could disappear and the time dependence of the interface shift could differ from the parabolic law.

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On the Growth Kinetics of Carbonitrided Layers for the Pure Iron : Modelling and Experimental Validation

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A mathematical diffusion model is applied for carbonitriding of the pure iron taking into account the diffusion of N and C through the α and ε phases and the thermodynamics properties of the Fe-N-C system. Analytical solutions are obtained for the ε monolayer growth of the compound layer assuming constant diffusion coefficients, and the simulation results are compared with those obtained from experimental data. It is shown that the phase constitution of the compound layer produced during carbonitriding of the pure iron can be predicted by this diffusion model and reasonable agreement is achieved between calculated

Long-Term Cyclic Oxidation Behaviour of Alumina- and Chromia- Forming Alloys

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Modern technology requires materials with significant capabilities to withstand high temperature degradation in the oxidising environment. FeCrAl steels are commonly used in a large variety of domestic and industrial applications. Examples of domestic use range from heating element foils and thin wires in cooking plates, radiation devices, toasters, microwave equipment, heaters in boilers and washing machines to heat exchangers, precision resistors in cars and surface treatment industry.

FeCrAl steels rely on their resistance against oxidation/corrosion upon the formation and maintenance of protective alumina scales. In spite of good thermodynamic stability of these scales unannounced component failure can occur during long term operation. The major life limiting factor is the aluminium reservoir (quantity of available aluminium) within the alloy which is required to form and maintain the stable alumina surface scale. After exhaustion of the aluminium reservoir, catastrophic component failure occurs due to breakaway corrosion/oxidation.

The model alloys and the surface treated materials were tested to evaluate physical properties, microstructural features, oxidation/corrosion resistance and life-time improvement. The correlation between alloy parameters and life time, as well as the modelling of oxide scale behaviour as a function of cycling conditions were studied.

Chemical and Pysical Iteractions of Si-rich Seel Substrates During Hot Dopping Experiences in a Molten Al-(25 wt%)Si Alloy.

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Fe-Si alloys are known to be excellent soft magnetic materials and their magnetic properties are optimised when the Si content reaches 6.5 Si wt%. At this Si content the alloy becomes very brittle because of ordering phenomena and special production routes have to be developed.

Among all the attempts diffusion techniques seem to be the ones with easier industrial applicability. Within this industrial frame a new diffusion route has been recently developed: hot dipping of Fe-Si sheets in a molten alloy of Al-Si and subsequent diffusion of both elements by annealing.

The chemical and physical interaction between Fe-Si alloys in the range 0-3.8 Si wt% and a molten Al-(Si 25wt%) alloy at 800 °C has been studied for different reaction times (from 0.1 to 200s) by hot dipping tests. Several intermetallic phases have been identified, Fe_2Al_5, $\tau1$-$Al_3Fe_3Si_2$, $\tau2$-$Al_{12}Fe_6Si_5$ and $\tau4$- Al_3FeSi_2, that already were reported in the literature dealing with the interaction between iron and molten Al-Si alloys. But in addition a new intermetallic phase appears Fe_3Si in contact with the Fe-Si substrate. Diffusion reaction and solidification phenomena appear involved in the developing of the coated samples. The growth kinetics have been studied and diffusion appears as the step controlling the intermetallic compounds growth. A relationship between the silicon content in the substrate and its reactivity with the alloy has been established. Special attention was paid to the effect of the microstructure of the dipped sheet on the interaction with the molten alloy. The higher deformated structures react faster; this effect can be explained by the faster diffusion through the high diffusivity paths like grain boundaries and dislocations.

Nitrogen Induced Formation of Nanostructured Precipitations in the Ti-W-C-N System

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A general trend in the field of hardmetals is to achieve a refinement of the hardmetal´s microstructures, usually by using submicron powders as raw materials [1]. In the production of WC-TiC-Co-based hardmetals the hard phase (Ti,W)C is an important starting material. In this study, an alternative route to produce this fcc hard phase with fine structures is investigated: nitrogen in-diffusion into (Ti,W)C hard phase leads to precipitations of tungsten-rich carbide phases [2]. The mechanism of precipitation (lamellar and labyrinth-like structures in the region of 100 nm) is thought do be discontinous segregation on the one hand and spinodal decomposition on the other hand. Hot-pressed (Ti,W)(C,N) samples of different compositions were annealed for various times at different temperatures and pressures in N_2 atmosphere. The composition and resulting structures of the precipitations were correlated with composition and stoichiometry of the hard phase as well as with annealing conditions. An outlook of a possible application of the observed phenomena to powder particles is given to achieve micron-sized particles of this hard phase with nanometer-sized structures as a raw material for fine-grained hardmetals.

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Simulation of Vacancy-type Complex Annealing in Phosphorus-doped Silicon

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Properties of silicon samples largely depend on their defect microstructure created during sample pretreatment. Information about the concentrations of some vacancy-type complexes (e.g. PV, OV, V_2) during annealing can be obtained by experimental methods, such as DLTS. These data are interpreted in terms of physical processes leading to transformations of complexes, such as thermal dissociation or long-range diffusion of complexes to sinks. The adequacy of these interpretations depends on the understanding of physical mechanisms of these processes. For example, it is not clear, whether the disappearance of vacancy-type complexes after annealing at 150-300°C should be attributed to direct complex dissociation, long-range diffusion of complexes or some other physical reasons.

In order to clarify the mechanisms of PV and V_2 annealing in *n*-type Si, we use a combination of ab-initio and lattice kinetic Monte-Carlo approaches. The density functional theory is used to find the binding energies and jump barriers for P-V and V-V pairs at different separations (up to the fourth coordination sphere) and in different charge states. In the case of PV-complex the preferable complex diffusion mode is through the ring mechanism, but at the mentioned temperatures it seems to be too slow to expect long-range diffusion. Divacancies are found to be very stable and their diffusion requires long atomic jumps (from the second to the fourth neighbour distances) with quite high migration barriers.

The mobility and interaction of vacancies and vacancy complexes is simulated by LKMC with event probabilities defined by the energy values from ab-initio calculations. Finally, a qualitative model for the estimation of the complex concentrations depending on annealing time, temperature, phosphorous content and initial vacancy concentration is discussed.

MD Simulation Study of B1-B2 Phase Transition under High Pressure: Effects of Defects

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Defects in the form of vacancies, grain boundaries and dislocations are known to affect the phase transition under high pressure. It was, however, difficult to directly discuss experimentally the transition process and the effects of defects due to the pico or nano second level phenomena. We had investigated the B1-B2 phase transition of KCl under pressure by MD simulation. In this study, we performed the MD simulation to discuss the effects of defects on the phase transition. The potential parameters used in MD simulation were empirically determined on the basis of Hugoniot data. The calculated results showed that the B1-type structure transformed to B2-type structure under hydrostatic compression, where the thermodynamic transition pressure was estimated to be 3.5 GPa in a perfect crystal. In the case of the existence of vacancies, it was found that when increasing vacancy concentration the phase transition pressure decreased almost to the thermodynamic transition pressure. In the case of the existence of a grain boundary, the phase transition occurred at the boundary and the phase transition pressure decreased nearly to the thermodynamic transition pressure by increasing the angle between the grains. In the case of the existence of dislocations, the B2 phase appeared around dislocations and the phase transition pressure decreased.

Kinetics of Phase Formations in the Al-Pt Thin Film System

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The initial phase formation resulting in amorphous and intermetallic phases has been investigated in Al-Pt system in order to analyse the aggregation of adatoms and synthesis of the first phase(s) depending on the local structural properties of the host Al film and Pt deposition rate. The thin films were prepared by a combinatorial method i.e. the continuous variation of the deposition rate and the quantity of the deposited Pt on the surface of first deposited Al film was realised by means of the shadowing method. The depositions were made at 250 °C substrate temperature on thin *a*-C layer supported by TEM microgrid. Varying the deposition rate of Pt between 0-1 and 0-0.05 nm/s it was found that the kinetics of the first phase formation strongly depends on the local properties of the Al film surface. The surface of the Al film is characterized by grain boundaries and monoatomic steps or bunches of steps which can be partially covered by an oxide phase formed by kinetic segregation during Al crystal growth. The pure grain boundaries and steps are the sources of the Al adatoms which react with Pt adatoms. Once Pt atoms are condensed on the surface as adatoms, they migrate, meet Al adatoms and form clusters. The cluster formation takes place preferentially in the area of pure surface sites and they composition corresponds to the intensity of Al adatom source (the rate of Pt source is constant).

At the 0-1 nm/s Pt deposition rates amorphous (a-Al_2Pt) grains form and their local number density shows the decorations pattern. At 0-0.05 nm/s Pt deposition rate the decoration pattern consists both of local density distribution and of various intermetallic Al-Pt phases (c-Al_2Pt, Al_5Pt, Al_6Pt). The presentation reports at first on a decoration pattern related to various phases. Subsequently, the detailed kinetics of phase formation and the development of decoration patterns are analysed.

Auger electron spectroscopical investigation of interfacial segregation in the Cu–Bi system

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Many important properties of materials are strongly influenced or even controlled by the presence of interfaces, such as grain boundaries (GBs) and free surfaces (FSs). Segregation of alloying elements at FSs as well as GBs has been observed in many systems. However, only in a few cases segregation of impurities at FSs and at GBs has been systematically compared. GB segregation in the Cu–Bi system has been investigated extensively by means of different techniques. Thus, GB segregation of Bi in Cu was exhibited by Auger electron spectroscopy (AES) and analytical electron microscopy. However, surface (FS) segregation of Bi in Cu–Bi alloys has been investigated only superficially because of the experimental difficulty posed by the high partial vapour pressure of Bi. Furthermore, according to the equilibrium phase diagram, the results presented in previous studies were obtained for Bi bulk concentrations above the solubility limit for the range of temperatures concerned, and hence cannot be attributed to a state of equilibrium for surface segregation.

Against the above background, a systematic investigation of segregation of Bi at both FSs and GBs in Cu, under identical conditions, is desired. Results of such a study are presented here. To avoid the problem of Bi evaporation upon Bi segregation at FSs a special method for sample preparation has been applied. Cu bicrystals containing deliberately made internal cavities at the interfaces were doped with Bi, annealed at temperatures between 1073 and 1223 K, and broken along the grain boundaries in an ultra-high vacuum chamber for AES. For the first time, surface segregation of Bi in Cu has been determined quantitatively applying AES to a bicrystal fractured along the GB. In the ranges of temperature and Bi bulk composition applied in this work the segregation at the free surface was found to be stronger than the segregation at the grain boundary.

Phase Transformations in ε-/γ'-Iron Nitride Compound Layers in the Temperature Range of 593 K – 693 K

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ε/γ'-Iron nitride (ε-Fe_3N_{1+x}, γ'-Fe_4N) compound layers with thicknesses of about 10 μm were grown on pure α-Fe by gas nitriding at 823 K followed by quenching. The nitrogen concentration profiles of these samples are the result of the diffusion of nitrogen into the solid, where local equilibrium can be assumed to govern the concentrations at the phase boundaries [1]. These samples were annealed at different temperatures in the range of 593 K – 693 K for different periods of time. These heat treatments lead to a redistribution of nitrogen within the solid samples; the annealing temperatures are sufficiently low to prevent (irreversible) loss of N_2 into the atmosphere [2]. The changes in the distribution of nitrogen were analysed by light microscopy, electron probe microanalysis and X-ray diffraction. These changes can induce changes of thickness of the ε- and γ'-sublayers as well as of the total compound layer [1]. Two main processes can explain the (sub)layer thickness changes: 1) Establishment of equilibrium (at the annealing temperature) within the ε/γ'-compound layer leads to a "backwards growth" of the γ'-sublayer accompanied by a nitrogen enrichment of the remaining ε-sublayer [3]. The overall compound layer thickness remains constant; 2) Formation of additional γ' from nitrogen of the ε-layer and iron from the Fe substrate which causes an increase of the overall compound layer thickness and consumes the ε-layer. Models of the phase transformations in the ε/γ'-iron nitride compound layers will be presented.

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Microstructural Characterization of TiAlSi Protective Coating Deposited on TiAlCrNb Alloy by Arc-PVD Method

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In this work results of microstructural investigations of aluminide coating modified by Si was presented. Protective coating (TiAlSi type) were deposited by Arc-PVD method in two steps (the deposition process was made by using PVT-550 Arc-PVD apparatus). In first step the AlSi adhesive layer was deposited on Ti-48Al-2Cr-2Nb alloy. The temperature of process, in this stage of coating deposition, was in range 200°C-400°C. In the second step the temperature of process in vacuum chamber was increased to T>700°C and, in consequence, the exothermal reaction between liquid Al-Si alloys and γ–TiAl phase was initiated. The time of this high temperature post-deposition treatment was 2 hours. After this 2- stages deposition process, TiAlSi type diffusion coating was formed. This type of protective coating contained two sublayers. Outside layer had a thickness 35µm and contained $TiAl_3$ phase modified by Si as main component. The small areas rich in Al and Ti-Si particles was found as well. The second layer was found as transition area between $TiAl_3$ outside layer and surface of TiAlCrNb substrate. The thickness of inside sublayer was 5µm. This area was build from "finger-like" grains of $TiAl_2$ phase and $TiAl_3$ rich in Si. The presence of $TiAl_2$ phase was a result of inward diffusion of Al from rich in Al outside layer and its reaction with γ–TiAl phase ($TiAl_{(s)} + Al_{(l)} \leftrightarrow TiAl_{3(s)}$). High concentration of Si (12% at.) in $TiAl_3$ phase in this layer was due to much smallest dissolubility of Si in $TiAl_2$ than in $TiAl_3$ phase. In consequence, during inward diffusion of Al and formation of $TiAl_2$ grains, the possibility of substitution of Al atoms by Si in this phase was much smaller. In effect, decreasing of Si concentration in $TiAl_2$, and increasing of Si concentration in $TiAl_3$ took place.

Refinement in the Mathematical and Numerical Treatment of the Internal Oxidation of Alloys

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When oxygen (O) dissolves from the atmosphere and diffuses into an alloy phase during oxidation, the less noble alloy components may react to form oxide particles within the metal. This process is termed internal oxidation. The refinement in the mathematical and numerical treatment is demonstrated for a binary alloy B-M. Metal B is assumed to be a noble metal under the oxidation conditions, i.e. no oxide of B can be formed. Metal M may form an oxide MO_ν. The reaction of dissolved oxygen (O) with M atoms in the alloy may be written as:

$$\mathrm{M} + \nu\mathrm{O} \rightarrow \mathrm{MO}_\nu .$$

The presented approach is based on the solution of the general diffusion equations for M and O coupled through the stoichiometry of reaction between oxygen, O, and the considered element. The main innovative contribution is the consideration of concentration dependent diffusion coefficients, concentration dependent source terms and arbitrary time-dependent boundary conditions formulated as a concentration, a flux or the mixed conditions. Furthermore, the finite dimension of the specimen is incorporated.

The numerical solution of the coupled diffusion reaction equations is based on a finite difference scheme. The considerable influence of concentration dependent diffusion coefficients, variable boundary conditions and finite dimension of the specimen on the propagation of the reaction front are presented for the system Pd-Mg and compared with classical solutions taken from the literature for constant diffusion coefficients, constant boundary conditions and semi-infinite specimens.

In-Situ Observation of Electromigration in Gold Nanowires

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We present electromigration measurements on thin gold nanowires obtained in situ in a scanning electron microscope (SEM). The wires are prepared using electron beam lithography (EBL) with widths well below one micrometer and lengths of several micrometers. The experiments are carried out at room temperature with current densities above 10^8 A/cm^2. During the electrical stressing of the wires we observe the nucleation and development of voids and hillocks in real time. The I/V – characteristics and the development of the resistance versus time can be directly assigned to morphological changes in the nanowires. The temperature change in the wires could be calculated due to the resistance change during the experiment and can be successfully separated from the morphological influence on the resistance.

Monte-Carlo Simulations of Diffusion in System with Sinks and Sources for Vacancies

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Vacancies play an exclusive role in diffusion of substitutional components from two reasons:

1. The mechanism of diffusion is based on exchanges of atoms with vacancies. This causes relatively complicated relations between diffusive fluxes and driving forces (gradients of chemical potentials of all components inclusive vacancies) given by the Onsager relation. Here the determination of Onsager kinetic coefficients represents the most complicated task.
2. The vacancies can be generated and annihilated at sources and sinks for vacancies. Climbing dislocations, grain boundaries or free surfaces can act as such sources and sinks. Their activity influences the conservation laws for all components and causes the vacancy wind connected with the deformation of the specimen known as the Kirkendall effect.

Recent Monte-Carlo simulations have been, to the knowledge of the authors, performed on system with no sources and sinks for vacancies. This, however, does not allow to test the diffusion laws in their whole complexity. On the other hand, the theory of interdiffusion is based on the assumption of dense ideal sources and sinks for vacancies, and, thus, it cannot be tested by recent Monte-Carlo models.

The aim of the paper is to present Monte-Carlo models for the treatment of diffusion in binary ideal-solution systems with sources and sinks for vacancies. Several strategies are proposed and evaluated. The results of Monte-Carlo simulations are compared with classical Darken's and Manning's theories of Kirkendall effect and related to the Onsager kinetic coefficients derived by application of Onsager's external principle in [1].

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Molecular Diffusion at the Water-membrane Interface

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Molecular dynamics of different molecules including peptides and molecular oxygen was studied. For this aim two types of model membranes were used– hydrocarbon (n-tetradecane) and lipid (1-palmitoyl-2-oleyl-phosphatidylcholine). Calculation of membrane dynamics was carried out in NVT and NPT ensembles (at isotropic normal pressure and at anisotropic, taking into account surface tension). The used thermostat based on collisional dynamics (frequency of collisions 10 ps^{-1}, mass of collisional particles 1 amu) and force-field proposed by Amber (Amber99) was applied. The following features of the membranes were considered: specific surface area and density of the media, diffusion parameters and parameters of lipid conformation. Also dynamics of molecules at water-membrane interface and in water was examined. Application of external linear field enabled the consideration of membrane penetration. This non-equilibrium approach allowed to find free energy profiles for different kinds of molecules. Structural (micro- and macroscopic) characteristics are found to be in a good agreement with experimental data. Some characteristics such as viscosity of media and diffusion coefficient of molecule in media were originally found. Dynamics of molecules at interface are determined by polarity, size and charge ratio. Free energy of transfer of charged molecules from water to membrane correlates with Born energy. Studies at different temperatures revealed that hydrophobic effect decreases with an increase of temperature.

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Diffusion studies of Na and Mg for the production of ISOL beams

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The isotope separation on-line facility ISOLDE at CERN produces radioactive ion beams by 1.4 GeV proton induced reactions in a “thick” target. For the release efficiency of short-lived isotopes, diffusion in the target matrix plays a central role. This work deals with the improvement of ISOL beams of the neutron-deficient isotopes $^{20\text{-}21}$Na and $^{20\text{-}23}$Mg, to be used for future experiments in nuclear astrophysics (with REX-ISOLDE) and collinear laser spectroscopy. These isotopes are best produced by spallation of close-by target elements, such as Al and Si. We studied the release of ^{7}Be, ^{24}Na and ^{28}Mg from the materials shown below by isochronical annealing of samples after activation with 1.4 GeV protons. The influence of surface desorption was studied by comparing with the release of shallow implanted 60 keV ^{24}Na and ^{28}Mg from the same host matrices.

Table 1 shows high-melting materials which have been studied in this work.

Table 1:

Material	Al_4C_3	AlN	Al_2O_3	Si	SiC	Si_3N_4	Ti	TiN	V
Melting point (°C)	2100	2200	2053	1410	2830	1900	1668	2950	1910

Off-line study of the mentioned samples will eventually allow the on-line application of targets made of the same materials.

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Ultraslow Motions in Crystalline and Amorphous Ion Conductors studied by Li Spin-Alignment Echo NMR

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Solid state nuclear magnetic resonance (NMR) has traditionally been a powerful probe for microscopic dynamics in condensed matter. Up to now, only few multidimensional solid state NMR experiments have been applied to study slow translational jump processes in Li ion conductors.

Spin-alignment echo NMR spectroscopy, which was developed to investigate dynamics of deuterons ^{2}H in organic materials [1], can be used to monitor extremely slow translational jump processes in the kHz to sub-Hz regime of spin-3/2 nuclei like ^{9}Be [2] and ^{7}Li [3] with quadrupolar couplings comparable to that of ^{2}H. The spin-alignment NMR experiment, which is based on the Jeener-Broekaert three-pulse sequence, takes advantage of the interaction between the quadrupole moment of the nucleus and the electric charge distribution in the neighbourhood of the nuclear site. The hopping induced change of the quadrupolar frequency ω_Q of a nucleus jumping between inequivalent sites with different electrical field gradients is used to trace ultraslow jump processes directly.

We will present results of spin-alignment NMR experiments on different Li ion conductors like Li_xTiS_2 (x = 1.0, 0.7), Li_4SiO_4, amorphous $LiNbO_3$ and Li_3N. Temperature dependent spin-alignment spectra as a function of evolution time t_p and single-particle two-time correlation functions $S_2(t_p, t_m)$ as a function of t_p and mixing times t_m yield information about microscopic dynamics as well as geometric properties of the diffusion pathways. The results are compared with those from classical relaxation NMR experiments.

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Growth Kinetics of the Intermetallic Phases in the Cu/In-Bi 22at.%/Cu Interconnection

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The protection of the environment and the progressive development of the electronic technology is the driving force for the investigation of new lead-free solders. The diffusion soldering process seems to be the suitable solution for joints production. The technology is unrivalled mainly because of the high thermal stability of the obtained interconnection accompanied by the relatively low joining temperature and easy preparation.

The study was focused on the application of the indium-bismuth alloy (melting temperature 72 °C) as an interlayer to join the copper substrates. The experiment was performed in the temperature range 85-150 °C. The presence of the $BiIn$ and $Cu_{11}In_9$ intermetallic phases (IPs) was detected after the short times of annealing. They were formed due to isothermal solidification reaction. The IPs are characterized by the higher melting temperatures (110 and 307 °C, respectively) then the used interlayer.

The investigation of the growth kinetics of the $Cu_{11}In_9$ phase was accomplished by measuring the width of the phase as a function of the annealing time. The use of the parabolic growth law formula allowed to find that the growth is controlled by the volume diffusion (an exponent factor was close to 0.5). At the higher temperature (150 °C) the morphology of $Cu_{11}In_9$ took the shape of scallops and the deviation from the parabolic growth was observed. This can be attributed to the fast diffusion through the grooves formed between these scallops, which get narrow after longer times of annealing (the diffusion slows down). The width of the $BiIn$ phase decreased with the annealing time. This was caused by the presence of the liquid in the interconnection zone, from that reason no kinetic studies was performed.

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Long Range Order Kinetics in Intermetallics with Varying Superstructure Stability

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"Order – order" reactions in an intermetallic compound are predominantly controlled by atomic jumps to the nearest – neighbour vacancies. An important factor controlling the dynamics of the processes is concentration of thermal vacancies on sublattice sites.

Extensive experimental investigations of long – range ordering (LRO) kinetics in ternary intermetallic systems of superstructure $L1_2$ were carried out. Two groups of compounds: $Ni_{75}Al_{25-x}Fe_x$ and $Pt_{75}Co_{25-x}Fe_x$, showing opposite relationships between the stability of $L1_2$ superstructure and concentration of Fe, were examined by means of isochronal residual resistivity.

The effect has been analyzed within the Schulze- Lücke formalism enabled separate estimation for vacancy formation E_F and migration E_M energies being components of the overall activation energy E_A for ordering kinetics. It was found out that in both systems an increase of activation energy E_A accompanying an increase of $L1_2$ superstructure stability is due the increasing tendency of the vacancy formation energy E_F, the activation energy for vacancy migration E_M shows either week decrease with x ($Pt_{75}Co_{25-x}Fe_x$) or no Fe-concentration dependence ($Ni_{75}Al_{25-x}Fe_x$).

Modeling of Phase Competition and Diffusion Zone Morphology Evolution at Initial Stages of Reaction Diffusion

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Problem of sequential phase growth in thin-film reactions remains unsolved despite numerous attempts of many authors. It is interrelated with the problem of morphology evolution at the initial stages of reaction. We present three new models of competitive nucleation and growth.

1. Kinetic Monte Carlo (kMC) simulation of simultaneous nucleation, competition and growth of two intermediate phases in A|B|A ... multilayer. The main peculiarity of the presented kMC-model is a strong dependence of interatomic interaction energies on the local atomic neighborhood, enabling us to distinguish more distinctly new phases. Dependence of phase competition on pair interactions and on the ratio of mobilities is analyzed.
2. Flux-induced lateral grain growth of new-formed IMC, leading to decreasing effective diffusivity, is investigated.
3. “Lateral” competition between nuclei of two IMCs (1 and 2) at the same interface A|B, is analyzed.

Diffusion of Silver in Silicate Glass and Clustering in Hydrogen Atmosphere

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Glasses containing silver nanoclusters are of interest for various applications in optical recording and communication. If a glass contains Ag^+ ions, annealing in a hydrogen atmosphere leads to the reduction of silver to the metallic state (Ag^0) and to the formation of silver nanoclusters. In this paper we study the kinetics of clustering during hydrogen diffusion into the glass and diffusion of Ag^0 atoms in the glass matrix.

Silicate glass plates were doped by Ag^+ ions to various depths in an ion exchange process. The samples were annealed in a hydrogen atmosphere a temperature ranging from 160 to 200°C. Reduction of the silver during diffusion of hydrogen into the glass was accompanied by growth of silver clusters, both in the bulk and on the surface. At subsequent stages of the annealing the optical absorption and reflection spectra were measured, as well as the cluster growth kinetics at the surface of the samples (by AFM). The absorption spectra have a peak near 410 nm corresponding to the surface plasmon resonance in Ag clusters. The position of the peak moves with the cluster growth. The theoretical analysis of the absorption spectra allowed us to estimate the cluster size as a function of time, as well as the thickness of the layer filled by clusters, which also changed with time. From the AFM data we could measure the kinetics of cluster growth on the surface. We have theoretically analyzed the kinetics of cluster growth during reactive hydrogen diffusion and found relations for determination of Ag^0 diffusion coefficients from the kinetics of bulk cluster growth, surface cluster growth, and thickening of the layer filled by clusters. Diffusion parameters both for Ag^+ and Ag^0 are measured and discussed.

Direct Force on Migrating Hydrogen in Metals

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The driving force on a proton in a metal due to an applied electric field is composed of two contributions, a direct force due to the charge of the proton and a wind force due to transfer of momentum of the current carrying electrons to the proton. The wind force is a quantity that has been calculated reliably for many systems with *ab initio* methods for the electronic structure. This has been done not only for migration of interstitials such as hydrogen, but also for substitutional impurities, including self-electromigration [1]. The direct force has been the subject of a long-standing controversy. Since about 1985 a consensus has been reached, and the screening of the direct force was considered to be small [2]. Nevertheless, Friedel and Nozières kept defending the vision that only a wind force was operative, and that the direct force was screened out. We will report about recent work in which it has been shown that the consensus point of view is correct. The formulation used is much simpler than what has been used earlier, by which now even Nozières has accepted the result. Friedel still doubts, but when we present our work he may have accepted the consensus point of view as well. That would imply that the controversy has been settled.

The new formulation even allows for an explanation of a measured result, which up to now has not been understood. For most hydrides a direct valency has been measured for the hydrogen as being of the order of unity. However, in *Nb(H)* a direct valency was found to be of about 0.44. We will show how such a deviating value may arise due to multiple scattering effects of the electrons around a proton surrounded by metallic atoms.

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Kinetics of Competitive Phase Growth in Cu-Ni-Sn System

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The kinetics of competitive phase growth in multiphase binary systems Cu-Sn and Ni-Sn and an effect of third substitutive component (Ni or Cu respectively) have been studied experimentally and analyzed theoretically. The diffusion couples were composed of contacting plates of Cu-Sn, Ni-Sn, or Cu/Ni homogeneous alloy-*Sn*. The Ni and Cu concentrations in the alloys varied from 25 to 75 at. %. The samples were annealed in temperature range 160-220°C in purified Ar atmosphere. In the binary systems Cu-Sn and Ni-Sn, from all phases allowed by the phase diagram, only relatively low-melting compounds formed and grew: Cu_6Sn_5 (η-phase, T_m = 415°C), Cu_3Sn (ε-phase, T_m = 676°C), and Ni_3Sn_4 (T_m = 795°C). All phases grew "unipolarly" as a result of Sn diffusion through the growing phase layer. The Sn concentration in the growing phases was higher than the stoichiometric one. The kinetics of the phase growth was parabolic, indicating diffusion regime of the phase growth. Theoretical analysis of kinetics equations for "unipolar" competitive phase growth allowed us to calculate interdiffusion coefficients $\widetilde{D}$ and Arrhenius equations for competitive phases Cu_3Sn and Cu_6Sn_5. In the diffusion couples Cu/Ni alloys - Sn the ternary phases $(CuNi)_6Sn_5$ and $(NiCu)_3Sn_4$ were formed and grew depending on the Cu/Ni ratio in the initial alloys. The principal features of the phase growth both in binary and ternary systems are low diffusion activation energy and thus high values of "dynamic" interdiffusion coefficients in the growing phases. The obtained results are discussed taking into account directed vacancy fluxes during reactive diffusion and disordering caused by concentration gradients, non-stoichiometric composition and insertion of substitutive elements.

An Alternative Treatment of Diffusion and Thermomigration

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Solute diffusion is a process of atoms jumping between sites and must therefore be describable in those terms as a conceptual model from which the quantitative behaviour can be predicted. However, this simple premise leads to a somewhat different paradigm from that which is adopted as standard in textbooks, whereby the diffusion coefficient varies with concentration according to Darken's thermodynamic factor. The proposed result of the conceptual model is that the diffusion coefficient should also be proportional to the activity coefficient. Indeed, various other authors have wondered about proposed, or even implicitly assumed formulations equivalent to this alternative paradigm in the past. The best test case would be of a dilute, interstitial element in a simple host lattice, for which the system thermodynamics have been well quantified and for which accepted experimental results from diffusion experiments already exist. Just such a system is carbon in fcc-iron, and the alternative treatment gives much improved agreement with experiment, yielding excellent agreement from 0 to 5 at.%C and 750 to 1300^{o}C, without the need for any empirical fitting of the frequency factor and/or enthalpy of migration as functions of concentration. This fully quantitative agreement is obtained with isothermal data. In the presence of a temperature gradient, there is an accepted formulation but no generally accepted conceptual model for the additional influences. Empirical fitting of a "heat of transport", Q^*, term is required, but the alternative approach can explain why, intrinsically, most interstitial solutes tend to migrate towards the hotter regions (negative Q^*) whereas hydrogen tends to migrate towards the colder regions (positive Q^*). However, fully quantitative prediction of the effects of a temperature gradient is likely to involve interactions with the heat flux, beyond the scope of a simple conceptual model.

Field driven solid state reactions and the influence of grain boundaries

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Solid state reactions in functional ceramics are a frequent source of materials' degradation. During working conditions functional ceramics used in electronic devices or solid oxide fuel cells are subjected not only to high temperature but also often to high electric fields. In addition to the chemical potential gradient an external electrical field acts as a second driving force for mobile components and modifies the kinetics. A prerequisite for solid state reactions is matter transport in the volume phase but also in internal interfaces. The latter pathway becomes even more important in nano- and mesoscaled systems. Due to the ongoing miniaturisation which is required in modern applications, the fraction of interfacial regions is also increasing. In contrast to matter transport in the volume phase, the structural influences on the atomic transport mechanism in interfaces are more complex.

The specific influence of interfacial ionic transport on electric field driven solid state reactions is demonstrated in the system $MgO/MgIn_2O_4/In_2O_3$. The interface where the reaction takes place becomes highly irregular due to diffusion in grain boundaries. An analysis by linear transport theory indicates that the transference number of cations in large angle boundaries of $MgIn_2O_4$ differs significanly from the bulk phase. In addition to the latter results, experiments on the ionic transport in ZrO_2/Al_2O_3 multilayers show a definite decrease of the activation energy for the transport of oxygen ions in the ZrO_2/Al_2O_3 interface.

For large lattice misfits in phase boundaries or large angle grain boundaries the interfacial structure may differ significantly from the volume phase. This can result in completely different transport properties. The experiments demonstrate the strong influence of interfacial transport on electric field driven state reactions on microscopic length scales. Differences in transport properties between the volume and interfacial regions are highly amplified in the presence of the second driving force.

Kinetics Constraints in Diffusion

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In the presence of strong external fields and steep gradients the flux formulae are not linear. The relation between the flux and the diffusion coefficient must be modified. The different flux-limited theories are presented. The flux formulae for solid systems far from equilibrium are derived and different forms of phenomenological flux limiters are discussed.

Random Walk Model of the Mechanical Relaxation

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A modified approach to the continuous time random walk model is discussed in the framework of the relaxation phenomena in the mechanical systems. The model applies to the defects migrations that results in the universal power-law behaviour of the stress and strain relaxation responses. The main stress is put on the derivation of the scheme leading to the widely used Kohlrausch-Williams-Watts function and its relationship with the frequency domain biparabolic function.

Diffusion in Network Structures

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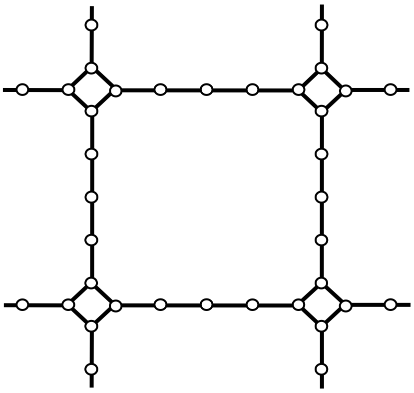
We consider diffusion in structures which are networks of small two or three dimensional atomic clusters connected by one dimensional chains of atoms. This diffusion model can be useful as a model for different diffusion processes: diffusion of alkali ions, diffusion along dislocation networks, grain boundary diffusion etc. Diffusion coefficients and correlation factors for different claster configurations are calculated. Results of theoretical calculations were supported by Monte-Carlo simulation.



Network structure
(example)

Peculiarities of Discontinuous Precipitation in the Pb-Sn Alloy

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Ambiguity of the solution is an important problem of the irreversible diffusion evolution in the binary and multicomponent systems during the phase transformations. In this case the different regimes corresponding to same initial and boundary conditions are possible. Discontinuous precipitation is one of such problems. Formal steady-state solution of this problem includes an invariant which is equal to a product of the squared structure period and the growth velocity. How does nature choose the values of period and velocity, is still not clear.

We are presenting a model of discontinuous precipitation in binary polycrystalline undercooled alloys. The basic mechanism in our description is the diffusion-induced migration of grain boundaries caused by grain-boundary diffusion in the moving transformation front. In our approach we independently and unambiguously determine the basic parameters: interlamellar spacing, speed of phase transformation front and supersaturation ahead of transformation front. We use equations for: 1) diffusion mass transfer in moving grain boundary; 2) balance of the entropy fluxes in the moving transformation front; 3) criterion of the maximum velocity of the free energy dissipation. In the frame of this model we find the concentration profile in the precipitating lamella and extent of the decomposition. Comparison of theoretical predictions with experimental results in system Pb-Sn at different super-saturations is carried out.

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On the Pressure and Temperature Dependences of the Self-Diffusion Coefficient for Simple Liquids

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A phenomenological theory developed by A.A. Smirnov for the self-diffusion and shear viscosity in monatomic liquids is considered from a standpoint of thermodynamical-fluctuation theory without any geometrical-model premises. It is only assumed that transport results from the movement of atoms within small and variable distances because of local thermodynamic-potential density fluctuations. The following expressions are analysed for the self-diffusion coefficient, $D(p, T)$, and dynamic viscosity one, $\eta(p, T)$:

$$D \cong AT^5/(e+vp-sT)^5 \text{ and } \eta \cong B(e+vp-sT)^5/T^4$$

where the ‘microscopic’ parameters $A \approx \text{const} > 0$ and $B \approx \text{const} > 0$, and, within the limited p–T-range, the smooth thermodynamical variables (as functions of pressure, p, and temperature, T) $s \cong \text{const}$, $e \cong \text{const}$, and $v \cong \text{const}$. These formulae are compared with experimental results with an agreement being generally quite satisfactory. Thus, *e.g.*, the following numerical relationships between the ‘constants’ A, B, s, e, and v are estimated on the basis of available reference data for liquid Ar (with atomic radius $r_{\text{atom}} \approx 1.91$ Å; $T_{\text{melting}} \approx 83.85$ K, $T_{\text{boiling}} \approx 87.25$ K at $p \approx 0.1013$ MPa): $AB \approx 3.83\cdot10^{-15}$ J/(m·K), $Bs^5 \cong -2.4\cdot10^{-10}$ Pa·s/K, $Be^5 \cong 7.5\cdot10^3$ Pa·s·K^4, $Bv^5 \cong 2.5\cdot10^{-40}$ s·K^4/Pa^4 when T [K] $\in$ [90, 150) and p [MPa] $\in$ (0.134, 10]. The following numerical relationships of A, B, s, e, and v are also estimated on the basis of available reference data for liquid K and Rb with atomic (effective K$^+$ and Rb$^+$ ionic) radii $r_{\text{atom}} \approx 2.36$ or 2.38 Å and $r_{\text{atom}} \approx 2.43$, 2.48, or 2.52 Å ($r_{\text{ion}} \approx 1.52$ or 1.33 Å and $r_{\text{ion}} \approx 1.63$ or 1.47 Å); $T_{\text{melting}} \approx 336.56$ K and 311.85 K, $T_{\text{boiling}} \approx 1033.15$ K and 976.15 K at $p \approx 0.1013$ MPa: $AB \approx 3.81\cdot10^{-15}$ J/(m·K) and $3.82\cdot10^{-15}$ J/(m·K), $Bs^5 \cong -2.1\cdot10^{-10}$ Pa·s/K and $-2.2\cdot10^{-10}$ Pa·s/K, $Be^5 \cong 7.1\cdot10^3$ Pa·s·K^4 and $7.2\cdot10^3$ Pa·s·K^4, $Bv^5 \cong 2.1\cdot10^{-40}$ s·K^4/Pa^4 and $2.2\cdot10^{-40}$ s·K^4/Pa^4, when p [MPa] $\in$ (0.1, 345], T [K] $\in$ [345, 868) and T [K] $\in$ [337, 856) respectively. Such a comparison is also made using the experimental findings on the viscosity of liquid Hg, Na, Li, Bi, Sn, Pb, Al, Ca, Co, Ga, Au, In, Mg, Ni, Ag, Cs.

Direct Steady-state Simulation of the Phenomenological and Diffusion Coefficients for Interstitial Diffusion

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Diffusion in interstitial solid solutions is addressed using a lattice gas model in which nearest neighbor interactions determine the atom-vacancy exchange frequencies. Using steady-state Monte Carlo computer simulation methods, we determine the chemical diffusion coefficient in this model directly from the flux and the concentration gradient, and the phenomenological coefficient directly from the flux and the chemical potential gradient. The steady state simulation method makes use of combined petit and grand canonical ensembles in a single calculation. We also determine these transport coefficients from independent random-walk simulations of the jump frequencies, collective correlation factors. The thermodynamic factor is also calculated independently. In this way, we are able to explore the different formulations of Fick's First Law that have been discussed recently in the literature

Diffusion Under Stress in Interstitial Alloys. Theory and Simulation

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The understanding of the effects of pressure and strain on diffusion in solids is limited. To describe the stress influence on diffusion flows in interstitial alloys, we use an approach, developed earlier for the case of vacancy mechanism [1]. This approach, in opposite to most other known ones, takes into account the atomic structure in the neighborhood of the defect and the stresses that could modify the energy of a jumping atom through the displacement field not only at the atom site but also in a saddle position. Apart from this, it takes the shear stresses into consideration that can modify the rate of jumps through the displacement field at the site and saddle position. Stress fields alter the surrounding atom configuration and, as a consequence, the height of the activation barrier is changed. Knowing these changes it is possible to calculate the jump rate and to obtain the equations for the interstitial diffusion fluxes. We obtained some equations for different kinds of interstitial atom jumps in FCC and BCC structures. Components of the diffusion coefficient matrix depend nonlinearly on the deformation tensor components. These dependencies are determined by coefficients depending on atom interaction. We developed a model for calculation of these coefficients in the framework of molecular static method taking into account an atom environment near the defect, as well as for the saddle-point configuration.

We used the obtained diffusion equations for studying interstitial redistribution near the defects, such as dislocation and crack tip. Modeling of interstitial segregation formation is taking into consideration both stress fields generated by defect and self-stresses. The simulation was done for the cases of H and C atoms in metals.

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^{65}Zn Diffusion in Pure and Al-Doped ZnO

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Zinc diffusion coefficients were determined in pure and Al-doped ZnO polycrystalline ceramics of high density (> 99% of the theoretical density). The undoped samples were prepared with ZnO powder of high purity (> 99.999%). Doped samples were prepared with two different contents of Al: 500 ppm and 3000 ppm. The polycrystalline samples were prepared by conventional sintering at 1400° C, for 4h, in oxygen atmosphere. These samples were resintered for 72h at 1393° C, in oxygen atmosphere, in order to increase the grain-size above 80μm. Samples of 17 mm x 17 mm x 3 mm were polished with diamond paste, and then submitted to a pre-annealing to equilibrate the samples with the temperature and atmosphere to be used in the diffusion annealings. The diffusion experiments were performed using the ^{65}Zn radioactive isotope as zinc tracer. The diffusion annealings with pure ZnO were performed from 1006 to 1377° C, in oxygen atmosphere, while the experiments with Al-doped ZnO were performed at the temperature of 1295° C, in oxygen atmosphere. The ^{65}Zn diffusion profiles were established by means of the Residual Activity Method or Gruzin's Method. Our results show that the zinc grain-boundary diffusion coefficients are ca. 4 orders of magnitude greater than the volume diffusion coefficients, in the same experimental conditions, which means that grain-boundary is a fast path for zinc diffusion in ZnO. It was also observed that the zinc diffusion is enhanced in Al-doped ZnO in regard with that in pure ZnO. Greater the Al content, greater the zinc diffusion coefficient. Analysis of the defect structure of the ZnO show that the zinc diffusion in ZnO takes place by means of an interstitial mechanism.

The Diffusion of Confined Polymer Chains

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Simple lattice model of polymer systems was developed and studied using the Monte Carlo method. The model chains were linear, star-branched with $f = 3$ arms and rings. The number of polymer segments in a chain was varied up to 1201. The chains were built on a simple cubic lattice with the excluded volume interactions only (the athermal system). The polymers were confined between two parallel impenetrable walls. A Metropolis-like sampling algorithm employing local changes of chain conformation was used. The dynamic properties of the model system were studied. It was shown that the long-time dynamic properties of the system (the self-diffusion) could be described by a master curve for chain lengths and distance between the walls under consideration. The differences in the mobility of chains with different internal architectures were shown and discussed.

On Vacancy Concentrations in Dilute fcc Alloys

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Bérces and Kovács [1] have estimated the vacancy concentrations $c_v(x)$ in dilute alloys taking into account V-*i*X complexes with *i* impurity atoms X in nearest-neighbour (NN) distance of the vacancy V and NN X-X interactions. The obtained approximation is based on the statistical arrangement of the impurity atoms in NN distance of the vacancy.

In thermodynamical equilibrium a redistribution of the impurity atoms has to be taken into consideration. This means that e.g. for attractive V-X interaction and repulsive X-X interaction arrangements with smaller numbers of impurity atoms in NN distance are preferred. In the present study the correct solution for the Gibbs free energy of vacancy formation for V-*i*X complexes is derived.

The improved model is compared with experimental data of $c_v(x)$ obtained with the aid of differential dilatometric investigations on dilute fcc alloys [2].

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Interdiffusion and the Kirkendall effect in ternary solid solutions

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Since the discovery of the Kirkendall effect, its various manifestations have been explored for binary systems in a great number of well-defined experiments. In general, it is accepted that the sum of the oppositely directed intrinsic volume fluxes of the components is equal to the velocity of the inert markers with respect to the laboratory-fixed frame of reference.

In the contrary, elucidation and rationalization of this effect in ternary systems are by no means trivial as it looks at first sight. A number of fundamental questions related to the behaviour of Kirkendall markers still have to be clarified. Does a "marker shift" (with respect to the laboratory-fixed frame of reference) exist in a ternary solid solution system? What may cause the marker migration in a ternary solid solution? Are there relations between magnitude of the marker shift and the corresponding diffusion path?

In this presentation the Kirkendall effect manifestations are discussed using examples of interdiffusion in the Co-Ni-Fe and Cu-Ni-Fe systems. A phenomenological treatment is introduced to rationalize marker behaviour in reaction couples exhibiting different "shape" of the diffusion paths on the isothermal cross-section.

Ab Initio Study of Self Interstitials in α-Zr

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The formation energies of self-interstitials in hcp-zirconium have been obtained from first principles electronic structure calculations in the framework of the density functional theory in the local density (LDA) and generalized gradient approximations (GGA) with supercells containing up to 97 atoms. Five configurations are found to have nearly the same formation energies. The most stable ones are the octahedral (O), split <0001> dumbbell (S), and basal octahedral (BO) configurations, with formation energies E_f^i=2.85±0.2 eV, followed by the basal split (BS) and crowdion (C) configurations, while the basal crowdion (BC) is unstable and decays to BO. The choice of the exchange-correlation functional affects mostly the non basal configurations, by an increase of ~0.2 eV within GGA. These calculations were first performed using a plane wave approach. In order to be able to investigate the effect of supercell size and migration mechanism, we have then developed an appropriate localized basis set for Zr adapted to the SIESTA code. The relative stabilities are very similar within both approaches.

Diffusion of Boron in Silicon and Silicon-Germanium in the presence of Carbon

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The ability of C to suppress B diffusion in SiGe semiconductors is exploited to obtain good effect during the fabrication of high performance Heterojunction Bipolar Transistors. In this study, this retardation effect of C has been studied by measuring B diffusion in four different kinds of MBE-grown layers: (i) pure Si , (ii) Si with a carbon peak (Si:C), (iii) SiGe and (iv) SiGe with a carbon peak (SiGe:C). The Ge concentration in (iii) & (iv) and the peak C content in (ii) & (iv) were ~12% and ~0.1%, respectively. To achieve non-injection conditions during annealing, sample surfaces were protected with dual silicon nitride + silicon oxide layers which had been deposited by low temperature processes. Diffusion anneals were performed using rapid thermal annealing (RTA) at temperatures between 940-1050°C in an O_2 atmosphere.

Concentration profiles before and after the anneals were measured using Secondary Ion Mass Spectrometry (SIMS) and using these, diffusion coefficient of B in each type of matrix were extracted by computer simulation. In the temperature range studied, diffusivity (D_{matrix}) varies as follows: $D_{\mathrm{Si}} > D_{\mathrm{SiGe}} > D_{\mathrm{Si:C}} > D_{\mathrm{SiGe:C}}$. This relationship shows that both Ge and C are contributing to the suppressing of B diffusion in Si, the effect of C being more profound. The combined effect of C and Ge reduces B diffusivity in Si by more than an order of magnitude. During RTA at 1000°C we also found that in SiGe, B diffusivity decreases with the C content.

A Path-quenching Scheme for Identifying Saddle States in Diffusive Dynamical Systems Involving High Energy Barriers

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Transition path-sampling is a recently introduced method which allows to study rare events by sampling the ensemble of transition pathways connecting two energy basins without knowledge of the reaction coordinates, the diffusion path or even the diffusion mechanism.

In the context of this methodology, we present new developments that consists of direct simulation of the mechanical action of the path describing the diffusive process from the view point of statistical mechanics. We show how the method can be used to construct diffusion pathways involving high energy barriers as commonly encountered in materials science.

Numerical Estimation of Point Defect Distribution Generated During Dopant Diffusion Using Irreversible Thermodynamic Theory

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The dopant diffusion is always related with native defect structure involving vacancy (V) and interstitial (I). The determination of point defect distribution is very difficult due to low concentration of point defect. So far, there are very few experimental as well theoretical data, concerning defect distribution generated during dopant diffusion.

This paper describes some theory development of simultaneous diffusions, mutual interactions of boron dopant and point defect (I, V) using irreversible thermodynamic theory. Based on the developed simultaneously diffusion equation system the numerical solution of dopant and point defects (Vacancy and Interstitial) distribution were calculated based on C^+ and Pascal language on PC. The distribution profiles of dopant and point defect are presented and discussed depending on different diffusion condition.

Modelling of Interdiffusion and Reactions at the Boundary; Initial-value Problem of Interdiffusion in the Open Systems

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The extended model for selective and concurrent oxidation of multi-component alloys is presented. The model basees on Darken's method for multi-component systems and allows modelling of interdiffusion when reactions at the boundary are present. It is postulated that the total mass flow is a sum of the diffusion and the drift flows. The Nernst-Planck's flux formula assuming a chemical potential gradient as a driving force for the mass transport is used for computation of the diffusion flux in non-ideal multi-component systems. The kinetic constrain for the fluxes at the boundary is introduced. This allows to avoid non-physical values of the interdiffusion fluxes.

This model enables prediction of the evolution of components distributions due to oxidation/sulphidation. For illustrating its capabilities modelling of the selective oxidation of Ni-Pt alloys is presented. The results are compared with those obtained from Wagner model. For the longer times both models give exactly the same results. InWagner model the equilibrium concentration of the elements at the boundary is reached instantly while in the presented model it changes with time. Consequently the model allows modelling of initial stages of oxidation process.

Numerical Analysis of Interdiffusion in Multi-Component Systems

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In modern mathematics and its applications in science we increasingly more often resort to generalized definition of a solution when the phenomena is described by the PDEs. Here by generalized solutions we understand functions that satisfy some integral equation which is equivalent to the original differential equation. However, this equivalence is limited only to some regular class of functions. There are several reasons why weak solutions are used.

- The existence of a solution is easier to prove
- Complex physical phenomena can be described
- Powerfull numerical schemes are available. Some of them (e.g. finite element methods) are the most powerful tools now available in applied mathematics

Generalized definition of interdiffusion problem (Darken method for multi-component systems) is presented. Numerical solution using finite element method (Galerkin's approximation) is shown. Some numerical aspects of the solution are discussed.

Mathematical Modeling of Solid-State Interdiffusion during the Mechanical Alloying Process

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It is known experimentally that the rate of solid-state diffusion increases significantly under the action of intensive periodic plastic deformation at relatively low temperature: the apparent diffusion coefficient reaches a value close to that in liquid metals (~10^{-5} cm^2/s). This is especially noticeable in Mechanical Alloying (MA) which presents a versatile means for producing a wide range of far-from equilibrium materials with unique properties. However, despite a large amount of experimental data accumulated in literature, a rigorous model of solid-state diffusion in the conditions of periodic plastic deformation has not been developed so far.

In this work, a new mathematical model of solid-state interdiffusion in a binary substitutional system A-B during periodic plastic deformation is developed. The model includes basic physical factors responsible for the observed increase of the diffusion rate, viz. generation of non-equilibrium point defects by gliding screw dislocations during deformation and point defect relaxation due to interaction with edge dislocations and vacancy-interstitial recombination. Cross-link interaction of the diffusion fluxes and the increase of partial diffusion coefficients due to non-equilibrium vacancy concentration is also accounted for. Besides, interaction of point defects with incoherent phase boundary A/B is included in the model.

Mathematical modeling has been performed taking into account realistic parameter values (e.g., self-diffusion coefficients measured in quasi-equilibrium conditions) and the process parameters typical of MA in a vibratory SPEX mill. A repeated “deformation-rest” cycle during MA is considered. The results of modeling are presented, and the physical mechanism of the enhancement of solid-state interdiffusion by intensive periodic plastic deformation is determined.

Measurement of the Impurity Diffusivity of Cu in Fe by Laser Induced Breakdown Spectrometry

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In the case of impurity diffusion studies, the diffusivity has been successfully measured by several methods such as Auger Electron Spectroscopy(AES), Secondary Ion Mass Spectroscopy(SIMS) and Rutherford Backscattering Spectrometry(RBS) for analyzing concentration penetration profiles when a suitable radioisotope is not available. In this study, a new technique Laser Induced Breakdown Spectrometry (LIBS) is applied to measurements of impurity diffusion coefficients of Cu in Fe. The volume diffusion coefficients for Cu impurity diffusion in α-Fe found in this work are in good agreement with previously published result obtained by SIMS measurements (Feller et al., 1977). The grain boundary diffusion coefficient $s\delta D_{gb}$ was also calculated by using the volume diffusivity and processing the tails of the measured profiles. The temperature dependence of the grain boundary diffusion coefficients can be expressed by linear Arrhenius equation. The values of activation energy for volume and grain boundary diffusion were about 260 and 180 $kJmol^{-1}$, respectively in the temperature range of 1103 to 1113 K. More reliable activation energy will be obtained through the detailed experiments in the wide temperature range. Also the magnetic transition effect on impurity diffusion of Cu in α-Fe will be discussed.

Diffusion in the High-temperature Material Molybdenum Disilicide

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Results from diffusion studies of silicon and molybdenum self-diffusion and of germanium heterodiffusion in molybdenum disilicide are presented. Diffusion of ^{99}Mo and ^{71}Ge was studied with the conventional radiotracer technique. Diffusion of silicon was studied after an implantation of the isotope ^{31}Si using a novel radiotracer method for measuring diffusivities of short-lived radioisotopes. ^{31}Si was produced and implanted at the ion-guide separator on-line device (IGISOL) of the University of Jyväskylä in Finland. Diffusivities were determined for both principal directions of the tetragonal molybdenum disilicide single crystals. Diffusion of silicon and germanium proceeds at similar rates, whereas molybdenum diffusion is slower by several orders of magnitude. Diffusion parallel to the tetragonal axis is slower than perpendicular to it for all three diffusants. The results indicate that diffusion in the molybdenum and silicon sublattice is decoupled and occurs by independent sublattice vacancy mechanisms. Together with theoretical calculations of correlation factors the results provide fairly detailed insight in the diffusion properties of the relatively complex intermetallic compound molybdenum disilicide.

Atomistic Modeling of Diffusion in gamma-TiAl

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Diffusion in the γ-TiAl compound ($L1_0$ structure) has been studied by kinetic Monte Carlo (KMC) simulations with vacancy jump rates computed with an embedded-atom method (EAM) potential. The EAM potential was obtained by fitting to a large database of experimental and first-principles data. The equilibrium vacancy and antisite concentrations on the sublattices are computed as function of temperature and composition within the lattice gas model of non-interacting point defects, with the defect formation entropy accounted for in the harmonic approximation. The rate constants of vacancy jumps are calculated within the harmonic transition state theory. The vacancy jump barriers are determined by the nudged elastic band method while the attempt frequencies are derived from the normal vibration frequencies of the simulation block in the equilibrium state and at the saddle point.

The KMC model includes both inter and intra-sublattice vacancy jumps, in each case for exchanges with either a regular atom or an antisite. It also includes configurations representing the effect of a neighboring antisite on a vacancy jump. The KMC simulations combined with calculated vacancy concentrations deliver the tracer diffusion coefficients of Ti and Al as functions of temperature, composition and diffusion direction, as well as the respective jump correlation factors and other diffusion characteristics. The results compare reasonably well with published experimental data measured on single-crystalline samples. The work establishes a methodology that can be applied to other ordered intermetallic compounds in the future.

First Study of Iron Self-Diffusion in Fe_2O_3 by SIMS

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In this work, the iron diffusion coefficients in Fe_2O_3 were determined by means of a non-radioactive method, by using the ^{57}Fe stable isotope as iron tracer. The experiments were performed using natural single crystals of Fe_2O_3. The diffusion specimens were cut with the dimensions 1mm x 4mm x 4mm, polished with diamond paste, and then submitted to a pre-annealing in order to equilibrate the samples with the temperature and atmosphere to be used in the diffusion annealings. Then a thin film of ^{57}Fe was deposited on a polished surface of the Fe_2O_3 sample. After oxidizing the iron film for short time at low temperature, the diffusion annealings were performed from 800 to 1100° C, in oxygen atmosphere. The ^{57}Fe diffusion profiles were determined by secondary ions mass spectrometry (SIMS), using a 10keV Cs^+ primary ion source. The diffusion profiles of the ^{57}Fe were established from the signals of the negative secondary ions $^{54}Fe^-$, $^{56}Fe^-$, $^{57}Fe^-$, $^{58}Fe^-$, using the expression: $C= I(^{57}Fe^-)/[I(^{54}Fe^-)+I(^{56}Fe^-)+I(^{57}Fe^-)+I(^{58}Fe^-)]$. The depth profiles were determined assuming a constant sputtering rate and measuring the depth of the craters by means of a profilometer Tenco. The diffusion profiles were measured perpendicular to the c-axis of the Fe_2O_3 single crystal. Two experiments, at 1000° C and 1100° C, were performed to measure the iron diffusion coefficients paralell to the c-axis in order to check the effect of the crystallographic direction on the iron diffusivity in Fe_2O_3. The results obtained are analysed, discussed and compared to previously published data determined by means of radioactive methods.

Tracer Diffusion and Ionic Conduction in Soda-lime Glasses

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Measurements of the tracer diffusivity and electrical conductivity have been made in two different high quality soda-lime silica glasses in the temperature range between 473 and 760 K. The tracer diffusion coefficients of ^{22}Na and ^{45}Ca follow Arrhenius laws. They show a large difference in magnitude. The diffusivity of ^{22}Na is three or four orders of magnitude faster than the diffusion of ^{45}Ca. The ionic conductivity of these glasses was determined by impedance spectroscopy. The conductivity diffusion coefficient, D_σ, was deduced from the dc conductivity via the Nernst-Einstein relation. The temperature dependence of D_σ for both compositions follow Arrhenius functions. The activation parameters and pre-exponential factors for the tracer diffusion and conductivity diffusion were determined. The results of tracer diffusion and electrical conductivity are compared and discussed. The activation energy of the diffusivity of ^{22}Na ist almost as large as the activation energy of the conductivity. The conductivity of these glasses is due to the diffusion of sodium ions.

The Superposition Method of Thin Layer Stochastic Dissipation and its Application to the Light Elements Diffusion Problem in Finite Space

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The solutions of diffusion equation are found analytically only for very simple and regular initial and boundary conditions even in the case of one-dimensional diffusion with the constant diffusion coefficient. At the same time a lot of real situations with the arbitrary initial distribution of diffusing elements are of great interest, particularly, in the case of relaxation processes in the wall materials of Dense Plasma Focus devices where the initial distributions of light elements (hydrogen, deuterium etc.) are usually after shots essentially non-regular.

A new method for numerical solution of such kind problems is presented. The idea of the model is based on superposition of stochastic dissipation of thin layers of diffusing elements. The solution of the one-dimensional diffusion equation in this case for the finite space, e.g. for a sheet with thickness *L*, was found. This solution was used then for modelling of the light elements diffusion (supposing that the diffusion coefficient is constant) in a sheet with arbitrary initial distribution of the diffusing element by summarising particular solutions for each thin layer at the given coordinate. .

The method was applied for the estimation of deuterium redistribution in thin surface layers of a steel sheet with initially non-monotonous distribution of the element. It was found that deuterium diffuses not only in the direction of the surface but also into the bulk of steel. For instance, if the diffusion coefficient is taken to be equal 10^{-11} m^2/s, the diffusion processes practically vanish after 1 millisecond and about a half of deuterium remains in the sheet.

MPI Assisted MD Calculation for Relaxation Processes in Fe-based Amorphous-like Structures

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Thin films of amorphous Fe-based alloys are now used as magneto-optical disks. They are great prospects of next-generation super high density recording media for DVD-RAMs and hard-disks. Study on the diffusion in thin films of amorphous Fe-based alloys is very important to the magneto-optical recording disks, because the amorphous films are pulse-heated repeatedly for the recording. During recording, the film surface on the disk is irradiated by a laser beam on an area with a diameter less than 1 μm, and cyclically heated and magnetized. The temperature rises over 500K. Therefore, quasi-stable amorphous Fe-based materials with high thermal stability for a long period are much desired. Using classical Molecular Dynamics (MD) algorithm and electronic co-worked networking technique of message passing interface (MPI) method, the present authors have made calculations to solve Newton's equations including all binary interaction potentials between Fe atoms and external forces in relaxation processes in amorphous-like structures.

In the present work, diffusion coefficients of Fe atom in the quasi-stable amorphous-like Fe-based structures during long-range relaxation processes have been calculated. The present authors have also applied covalent-type Si-like effects to a Fe-based amorphous-like structure and calculated the diffusion coefficients and the activation energy spectrum (AES). In addition, comparison between the activation energy for the diffusion and the AES of the structural relaxation processes has been made. Consequently, the addition of covalent-type effects improves the thermal stability of Fe-based amorphous-like structure for a long period. This is due to the strong covalent-type bonding. Another conclusion is that a strong relationship exists between the diffusivity of Fe atoms and the thermal stability in the quasi-stable amorphous-like Fe-based structures.

Nitrogen Diffusion in Deformed Iron and Iron-Based Alloys

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Diffusion saturation by nitrogen well known as nitriding is widely used in industry for the improvement of mechanical properties of surface layers of iron alloys and steel products. As a structure dependent process diffusion substantially depends on the presence of crystalline defects and non-equilibrium strained state of metal materials. Structural defects essentially affect diffusion of nitrogen in metals and phase formation processes. Such influence is explained by different character of interaction of interstitials (N, C) with non-mobile and mobile crystalline defects. One of the methods in this direction concerns application of chemical-thermal treatment in combination with plastic deformation.

In this work deformed α–Fe and Fe-Cr alloys after nitriding were investigated using metallography, electron microscopy, X-ray diffractometry, microhardness test and Mössbauer spectroscopy. It was established that nitrided layers consisted of nitride ε- i γ'- phases and α–solid solution of nitrogen in Fe and alloys. The existence of narrow regions of deformation 3-8 % and 20-30 % in which the accelerated (more then 2 times) formation ε- i γ'- phases in surface layer during nitriding was observed. The correlation of mechanical properties with diffusion layer structure, phase composition and thickness of nitride phases’ layers was found.

The *non-monotonous* dependence of thickness of ε- and γ'- phases on deformation degree results from different diffusion mechanisms of nitrogen in a deformed material. The greatest number of *mobile dislocations* is formed under the deformation of 3-8 and 20-30 %, which can provide the additional diffusion of nitrogen atoms in *Cottrell’s* atmospheres by *the dislocation-dynamic mechanism*. Such processes influence the kinetic of phase formation that results in the accelerated growth of ε- and γ'- nitrides and in the increase of microhardness of the surface diffusion layers.

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Ni^{63} Grain Boundary Diffusion in NiTi Shape Memory Alloy

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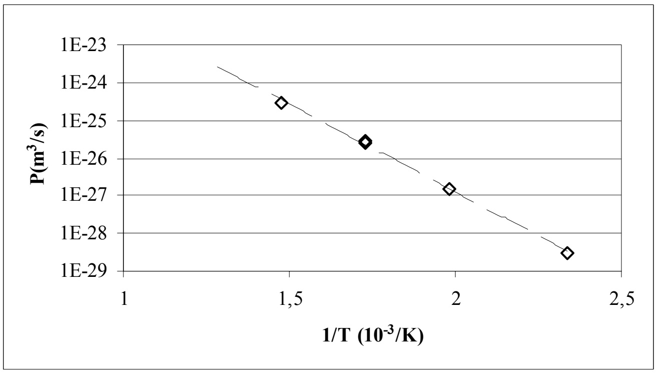
Ni^{63} grain boundary diffusion in polycrystalline NiTi B2-type shape memory alloy was investigated in the temperature range of 428-678 K. All the experiments were carried out in the kinetic regime type B. The samples were slightly Ti rich (49.93 at. % Ni and, 50.07 at. % Ti) and the grain size was of 150 μm. The temperature dependence of the triple product ($P=s\delta D_{gb}$) of the segregation factor (s), the grain boundary width (δ) and the grain boundary diffusion coefficient (D_{gb}) can be described by the following Arrhenius function:

$$P(T) = 2.6 \times 10^{-18} \exp\left[-(89000)/RT\right] \quad \mathrm{m^3/s}\ .$$



The Arrhenius-plot of the calculated triple products.

Mechanical Properties as a Function of Zinc Content, Degree of Cold Drawing and Annealing Temperature in α-Brasses

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Increasing Zinc content up to 28 wt. % Zinc was found to increase stress level and ductility. Degrees of cold drawing up to 99 % reduction in cross sectional area increased stress level while it decreased the ductility for the different Cu-Zn alloys studied. On the othe hand annealing after cold drawing increased the ductility but decreases stress level. The abrupt decrease in ductility was observed after high temperature annealing of highly drawn wires and especially for alloys with high Zn content.

The results were discussed according to current solid solution hardening mechanisms, roughening of slip planes, locking of extended dislocation and difficulty of cross slipping.

Self-diffusion of Iron in Fe-Zr Multilayers Measured with Neutron Reflectivity

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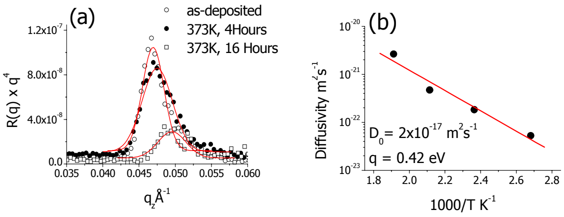
Neutron reflectivity (NR) is a technique,which can measure (self-)diffusion lengths, which is about an order of magnitude smaller as compared to conventional techniques e.g. secondary-ion mass-spectroscopy depth-profiling. Fe-Zr isotopic multilayers (MLs) samples with the structure Si/[FeZr(9nm)/^{57}FeZr(5nm)]$_{x20}$ have been prepared by co-sputtering of Fe and Zr using magnetron sputtering. In the as-deposited state the film has been found to be amorphous. The thermal annealing of the as-deposited film shows that up to the annealing temperature of 573K, the film remains amorphous and after annealing at 673K the film becomes nanocrystalline with an average grain size equal to 6nm. The self-diffusion measurements using NR in the MLs have been done after annealing the MLs below nanocrystallization temperature to achieve a constant diffusion length at each temperature by monitoring the decay of intensity at the Bragg peak arising due to isotopic periodicity(fig. a). It has been found that the diffusivity at different temperatures follows Arrhenius behaviour (fig. b) and the pre-exponential factor D_0 and the activation energy q are: $D_0=2\times10^{-17\pm1}$ m^2s^{-1}; q=0.42±0.1 eV. The activation energy and the pre-factor in the present case have been found to be significantly small as compared with the bulk diffusion at high temperature. As the activation energies of the vacancy-related diffusion processes are ~1.5 eV, it has been suggested that in the present case diffusion is mainly contributed by point defect concentration and their mobility.



Core-level and Valance Band Studies of the Pseudomorphic Growth of Tin on the Low Miller Index Faces of the InSb

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The high resolution ultra-violet photoemission spectroscopy (HRUPS) technique is used to study the development of the interfaces as a function of Sn coverage at different InSb surfaces [(110), (111), and (100)]. By analyzing the In 4d core-level and the valance band spectra we show the presence of some In-clustering on InSb(111) . For the InSb(100) surface we observe two surface components in the In 4d core-level spectra associated with the c(2x8) reconstruction. The absence of any surface reconstruction due to In atom interdiffused into the Sn layer is also discussed.

Grain-boundary Diffusion of ^{57}Co and ^{195}Au in Polycrystalline Iridium

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Grain-boundary diffusion (GBD) of ^{57}Co and ^{195}Au in polycrystalline iridium, which was prepared by deformation of a single crystal and its subsequent recrystallization, has been studied. The traditional sectioning of diffusion zones including measurements of "layer activities" has been supplemented with measurements of intensities provided by monoenergy hard and soft emission components of atomic probes from the remainder of the sample after part of the GBD zone is removed. From the intensity ratio of these components one may determine qualitatively the type of the depth distribution of the concentration (the profile) of atomic probes in the GBD zone. GBD is realized as a two-dimensional diffusion flow in polycrystalline iridium at homologous temperatures that are extremely low for FCC metals. The diffusion activation enthalpy Q_{GB} in the core of the grain boundaries (GB's) in polycrystalline iridium is lower than Q_{GB} in the GB core in polycrystalline tungsten in accordance with different homologous temperatures of these metals. The diffusion at low homologous temperatures of substitutional ^{57}Co and ^{195}Au atomic probes from the GB core to adjacent regions of the lattice, which contain a superhigh concentration of "vacancy – interstitial impurity" complexes, is due to "impurity" vacancies from the "vacancy – interstitial impurity" complexes.

Point Defects in Lattice Regions Adjacent to the Grain Boundary Core in Pd, Ta, W and Pt Polycrystals that Determine Pumping of Substitutional Components during Grain-Boundary Diffusion

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Regions of a high concentration of point defects (HCPD) are localized near the core of grain boundaris (GB’s). Their size in the direction perpendicular to the GB surface is about 1 nm. HCPD regions are formed during annealing under the technical vacuum even in nominally pure metal polycrystals. The composition and properties of HCPD regions are studied using the gamma resonance emission of ^{57}Co (^{57}Fe) atomic probes introduced in polycrystals by means of grain-boundary diffusion. The elemental composition of HCPD regions after annealing under the technical vacuum was determined from the parameter Λ_2 of the point defect quality. Oxygen–vacancy complexes are formed in HCPD regions of Pd, Ta, W and Pt during annealing under technical vacuum thanks to the diffusion of vacancies from the GB core. The composition of vacancy-oxygen complexes depends on the annealing temperature. The vacancy concentration of the complexes in HCPD regions of Pd, Ta, W and Pt is as high as 0.5 at.% already at a temperature of about $0.4T_m$ (T_m is the melting point of the matrix).

Pumping of substitutional components from the GB core during the grain-boundary diffusion at low homologous temperatures depends not on equilibrium vacancies, but on "vacancy–interstitial impurity" complexes in HCPD regions.

Formation Activation Enthalpies of Vacancy–Oxygen Complexes outside Grain Boundary Cores in Adjacent Regions of the Lattice of Pd, Ta, W and Pt Polycrystals and in Grain Boundary Cores In Cr, Ta and W Polycrystals

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Formation activation enthalpies $(Q^{f}_{Ovac})_{HCPDR}$ and $(Q^{f}_{Ovac})_{GB}$ of vacancy-oxygen complexes in lattice regions (HCPD regions) adjacent to the GB core and in the core of grain boundaries (GB's) have been determined experimentally for the first time. They were measured using Arrhenius dependencies of vacancy contributions $(\delta_{Vac})_i$ to isomer shifts δ_1 and δ_2 of two components in the spectra of NGR emission of ^{57}Co (^{57}Fe) atomic probes localized in two discrete regions of the grain-boundary diffusion zone, namely the GB core in Cr, Ta and W polycrystals and outside the GB core in adjacent lattice regions in Pd, Ta, W and Pt polycrystals. Similarly to enthalpies $(Q^{f}_{vac})_{vol}$ of vacancy formation in the bulk of these metals, enthalpies $(Q^{f}_{Ovac})_{HCPDR}$ and $(Q^{f}_{Ovac})_{GB}$ exhibit a linear dependence on the universal homologous temperature $V^{f} = 0.2T_m + 0.8\theta_D$, here T_m – melting point and θ_D – Debye temperature. The $(Q^{f}_{Ovac})_{HCPDR}$ и $(Q^{f}_{Ovac})_{GB}$ values approach the known calculated minimum values of the formation activation enthalpy of vacancies on special grain boundaries in Al, Cu and Mo.

Interdiffusion in Co/Ta Multilayer Thin Films

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Artificially controlled multilayers are of considerable industrial interest because of their specific (magnetical, optical, electronical) properties. Especially, Co/Ta layers are used in a part of spin valve that have Giant Magnetoresistance (GMR)effect. GMR read and write thin film heads requires thermally stable MR materials that can withstand heating cycles in excess of 523K during head fabrication. Thermal stability of GMR spin valve structure, i.e., interdiffusion at interface, is one of the most important problems. Intermixing at the Co/Ta interfaces causes a decrease in MR ratio and magnetic properties. However, there have been no reports on interdiffusion data of Co/Ta multilayer thin films. In this paper, we will discuss the stress release phenomena, structural relaxation and interdiffusion processes during annealing. The Co/Ta multilayers were prepared by dc magnetron sputtering on single crystal Si substrate. Base pressure and Ar pressure for sputtering were 1×10^{-6} Torr and 2 mTorr respectively. The Co/Ta multilayers were annealed for 0.2-80 hours at various temperatures (473K-673K) in vacuum (under 10^{-5}torr) furnace. The effective interdiffusion coefficients were determined from the slop of the best straight line fit of the first peak intensity vs. annealing time [d $\ln(I_{(t)}/I_{(0)})$ /dt] by X-ray diffraction (XRD) low angle measurements. The drastic decrease of the relative intensity in the initial stage shown due to the structural relaxation was excluded in the calculation of effective interdiffusion coefficients. The activation energy for interdiffusion was calculated from the slope of lnD vs. temperature by Arrhenius equation. For reference the change of magnetic properties (saturation magnetization and coercivity values) were measured by Vibrating Sample Magnetometer (VSM).

The Effect of Magnetic Field on Kinetics of Grain Boundary Grooving in Iron

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The kinetics of grain boundary grooving in polycrystalline iron was studied by scanning probe microscopy. It was shown that external magnetic field of 5 kOe slows down the kinetics of grain boundary grooving at 750 °C by about one order of magnitude. This observation is discussed in terms of recently discovered magnetic effect in surface diffusion [1]. Numerical estimates show that magnetic filed of this amplitude causes the same increase in spontaneous magnetization of iron that can be achieved by the decrease of temperature by approximately 10 °C. Being too small to cause any significant change of bulk self-diffusion, such increase in magnetization affects strongly the surface self-diffusion, since the magnetic effect for surface diffusion is much stronger than for the bulk one.

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Diffusion Mechanism of Pores Dissolving in Nickel-based Superalloys Under Hot Isostatic Pressing

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The mechanism is proposed of pores dissolving in monocrystals. The rate of the process is defined by bulk and intercrystalline diffusion under two possible forces: strain induced by hot isostatic pressures and surface tension induced by curvature of the pore. The estimations when practically for all pores sizes the first force is the main one show that the mean size of the pore decreases by the root square law. For nickel – based superalloys at the temperature range 1200 – 1300 ^{0}C the time of pores dissolving is of the order of some hours and is in good agreement with experiment.

Diffusion of Ion Implanted Hydrogen in Si_3N_4:H Films

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The tracer diffusion of ion implanted hydrogen ^{2}H is studied in amorphous and polycrystalline magnetron-sputtered Si_3N_4:H thin films with secondary ion mass spectrometry (SIMS) in the temperature range between 740 and 1050 °C. The experimentally obtained diffusion profiles are simulated by computer calculations based on the concept of trap limited diffusion where the tracer atoms form immobile complexes with (a) intrinsic film defects like dangling bonds and (b) extrinsic defects caused by the implantation damage.

For amorphous Si_3N_4:H films a high dissociation rate of intrinsic complexes is present and effective diffusivities are observed, which obey an Arrhenius behaviour with an activation energy of $\Delta E = 3.4$ eV and a pre-exponential factor of $D_0 = 5 \times 10^{-4}$ m^2/s. Pre-annealing of the amorphous films up to 1200 °C before the diffusion experiments in nitrogen does not significantly influence the diffusion. In contrast, experiments on films which were charged with hydrogen up to about 2.6 at. % show an increase of the diffusivities of about one order of magnitude, accompanied by a decrease of the activation energy to $\Delta E = 2.7$ eV and of the pre-exponential factor to $D_0 = 3 \times 10^{-6}$ m^2/s. Possible explanations for that behaviour are discussed.

For polycrystalline Si_3N_4:H films non-Gaussian depth profiles and time dependent diffusivities are observed, which indicates a change in the trapping behaviour, presumably due to the presence of grain boundaries.

Role of Cu at the Ni-Ag Interface on the Reactive Solid State Dewetting by Cavitation in the System Ag-Ni-O

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Recent results are presented showing that the presence of a thin copper layer deposited under ultra-high vacuum at a nickel-silver interface can suppress the process of reactive solid state dewetting by cavity formation, which was previously reported.

Indeed when thick silver films deposited onto Ni substrates are annealed at high temperatures in an oxygen atmosphere dewetting occurs because a NiO layer is formed at the Ag-Ni interface as a consequence of oxygen diffusion through the silver film. Cavity formation at the Ag-NiO interface had been shown to be the main mechanism of dewetting for short annealing times [1,2].

A study of the role of this interface layer in the control of the kinetics processes associated with NiO growth and cavity formation will be presented.

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Kinetics of Minority Carriers in GaN Epilayers Doped with Rare-Earth Elements

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An investigation of photoluminescence (PL) spectra, kinetics of decay and evolution of these spectra is an efficient method for studying behavior of introduced impurities. The investigations of the III-nitrides doped with rare-earth elements (REE) demonstrated the ambiguity of the results, that was caused by structural variety of the III-nitrides.

In the present paper several groups of the GaN epitaxial layers grown by MOCVD and HVPE have been investigated. REE (Eu, Sm, Er) was introduced from a surface source to the epilayers differing in structural peculiarities characterized by the different type of mosaic structure and different position of Fermi level.

It has been established from the kinetics of decay and evolution of the PL spectra and the Mössbauer spectroscopy that the REE behavior is defined by the defect concentration and the Fermi level position. For GaN epilayers with the high defect concentration, that manifests as disintegrated and non-relaxed domains, REE occupies domain boundaries. In this case the defect-related bands have been observed in the PL spectra. Moreover the gettering effect took place, which has not been observed in the epilayers with the low defect concentration. It has been established that the intensity of the intracenter *f–f* transitions in REE is larger for the GaN epilayers with lower concentration of defects.

Ellipsometric evidence of $CoSi_2$ formation in Co/Si multilayer induced by thermal annealing

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The work aimed at the demonstration of the potential of the spectroscopic ellipsometry approach for studying of the solid state reactions in (3.0 nm Co / 10.6 nm Si)$_{20}$ multilayered film (MLF), either spontaneous and/or induced by thermal annealing. The solid state reactions in the Co/Si MLF induced by thermal annealing were studied by using traditional structural X-ray diffraction methods and resistometry. It was shown that the structural changes in the as-deposited Co/Si MLF cannot be detected by X-ray diffraction tools - as-deposited Co/Si MLF is amorphous. However they confidently may be recognized by the optical methods. The regions with a stoichiometry close to Co_2Si are supposed to be spontaneously formed in the as-deposited Co/Si MLF. Sequential annealings of Co/Si MLF at 400, 600 and 700^0C produce visible changes in its amorphous-like high-angle x-ray diffraction spectrum. Thermal annealing at 400^0C of the Co/Si MLF causes the formation of the first Co_2Si phase. The second CoSi phase was detected in the Co/Si MLF by X-ray diffraction tools after its annealing at 600^0C. The spectroscopic ellipsometry also indicates the formation of the regions with a stoichiometry close to CoSi. The conclusion on the formation of $CoSi_2$ phase induced by annealing of Co/Si MLF at 800^0C can be confidently done on the basis of optical and X-ray study, as well as by means of resistometry.

Diffusion Impurity Drag of Incoherent Twin Grain Boundaries in Zn

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The role of impurities in grain boundary (GB) motion is well known. There are two ways to investigate the influence of impurities: using high purity material or studding the migration of 'special' GB, for example, twin GB. Single crystals of Zn were grown by directional crystallisation technique using high purity (99.995 at. % and 99,9995 at. %) zinc. Due to applied stress twins are introduced into a single crystal and, consequently, a bicrystal in the form of the loop between two coherent and one incoherent GBs is formed. The mobility of incoherent twin boundaries was measured *in situ*. It was found that kinetic parameters of incoherent grain boundaries are varied. There were observed three kinds of twin grain boundary motion. We supposed that three kinds of motion resulted from the difference in the absorption capacity. Stress and strain at twin GBs cause the difference in the absorption capacity. Compatibility stresses' will be generated during a heat treatment, namely when a bicrystal in form of a loop with two coherent and one incoherent GBs is heated or cooled. The stress effect on twin GBs depends on the type of GBs, GB plane orientation and temperature. During heat treatment adjacent grains change their dimensions according to the value of the product $\Delta a \times \Delta T$. These 'compatibility stresses' may be relieved if GB motion occurs. 'Compatibility stresses' play an important role in GB migration due to the interaction of lattice dislocations with GBs. This phenomenon causes GB dragging or moving, and as a result, activated motion, non-activated motion and transition from activated to non-activated motion with a jump-wise character are observed.

It is concluded that the kinetic properties of twin grain boundaries differ one from another because fitting Zn basic matrix to a twin establishes different GB impurity concentrations at twin GBs.

Crack Formation Induced by Grain Boundary Wetting

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Polycrystals of Cu and Al wetted by saturated melts of Bi and Sn were studied in temperature range from 400 to 600^0C and time range from 10 min. to 7 hours. The main grain size changed from 50 μm to 1 mm. The liquid channels of different depth and morphology were observed at grain boundaries.

The part of the channels (about 10%) was empty or partly filled by melt. The rate of growth for these channels was much greater than for the others. At the top of such channels dislocations etch pits were observed. By these reasons it is possible to assume these channels being the cracks formed along grain boundaries. The crack formation evidently is connected with diffusion of the melt into grain boundary. It causes the mechanical stresses due to difference between atomic volumes of diffusant and matrix.

The model of crack formation is presented. Using this model the average rate of the crack growth was estimated.

Analysis of the Time-Dependence of Atomic and Vacancy Concentration Profiles during Interdiffusion

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In this paper, we address the fundamental problem of chemical interdiffusion in binary alloys for the case where vacancies at non-equilibrium concentrations may be generated during the interdiffusion process. With the usually accepted space-time Boltzmann coordinate transformation there is a ’residual’ time-dependence observed for the atomic and vacancy profiles measured during interdiffusion experiments. To describe this effect we take a very general phenomenological approach to interdiffusion and develop it in a new way. Time dependence can be analysed in a strict way that is justified by the use of mathematically well-developed numerical methods. For the commonly encountered small vacancy concentration case our strategy centers on directing the information about the driving force associated with the non-equilibrium vacancies (which is effectively not measurable) onto the velocity of inert marker(s) in the diffusion zone. In this paper specific effort is made to answer the following question: ”Is it possible to predict if the vacancy concentration is at quasi-equilibrium during interdiffusion or not on the basis of the time-dependence of the obtainable concentration profiles?”

Reaction Kinetics at the Interface of Nickel with Liquid Bismuth and a 51Bi-42Sn-5In-2Zn Alloy

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Dissolution kinetics of solid nickel in liquid bismuth and a 51% Bi–42% Sn–5% In–2% Zn alloy and the formation of intermetallic-compound layers at the solid-liquid interface were studied. The saturation concentration or solubility, c_s, of nickel in bismuth was determined to be 0.32 mass% at 300°C and 0.39 mass% at 350°C. Appropriate values of the dissolution-rate constant, k, at an angular disc rotation speed of 24.0 rad s^{-1} are $1{,}5 \times 10^{-5}$ m s^{-1} and $4{,}0 \times 10^{-5}$ m s^{-1}. Much lower nickel solubility values were obtained for a 51% Bi–42% Sn–5% In–2% Zn alloy, namely, $c_s = 0.0053$ mass% at 300°C and 0.015 mass% at 350°C, whereas the dissolution-rate constant, being respectively $1{,}2 \times 10^{-5}$ m s^{-1} and $3{,}8 \times 10^{-5}$ m s^{-1}, does not differ considerably from that for nickel in bismuth. Evaluated diffusion coefficients of nickel into bismuth are $0{,}23 \times 10^{-9}$ m^2 s^{-1} at 300°C and $1{,}0 \times 10^{-9}$ m^2 s^{-1} at 350°C. Corresponding diffusion coefficients of nickel into a 51% Bi–42% Sn–5% In–2% Zn alloy are $0{,}17 \times 10^{-9}$ m^2 s^{-1} and $0{,}96 \times 10^{-9}$ m^2 s^{-1}. These values characterize the rate of transition of nickel atoms across the diffusion boundary layer at the solid-liquid interface into the bulk of molten bismuth or alloy. The intermetallic layer formed between nickel and bismuth is one-phase and consists of the $NiBi_3$ compound, though two compounds (NiBi and $NiBi_3$) are known to exist in the Ni-Bi binary system. Dissolution of the nickel base in liquid bismuth causes a manifold decrease of the layer thickness compared to the case where bismuth is saturated with nickel and therefore no dissolution occurs. The composition of the intermetallic layers formed between nickel and a 51% Bi–42% Sn–5% In–2% Zn alloy was found to be somewhat more complicated.

Mathematical Treatment of Diffusional Growth Kinetics of Two Intermetallic Layers

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Diffusional growth kinetics of two intermetallic or other compound layers are usually treated using parabolic equations of the type $x^2 = 2kt$. For sufficiently thick layers, these equations produce a quite satisfactory fit to the experimental data. In fact, however, growth kinetics of the A_pB_q and A_rB_s layers at this stage are more complicated and described by a system of non-linear equations (see V. I. Dybkov, 'Reaction diffusion and solid state chemical kinetics', The IPMS Publications, Kyiv, 2002)

$$dx/dt = k_A/x - (rg/p)\, k_B/y, \qquad (1_1)$$

$$dy/dt = k_B/y - (q/sg)\, k_A/x, \qquad (1_2)$$

where g is the ratio of molar volumes of the compounds. An obvious criterion for the applicability of these equations is a constancy of k_A and k_B over a given range of time. For the sake of illustration, the experimental data on growth kinetics of the Al_3Mg_2 (A_pB_q) and $Al_{12}Mg_{17}$ (A_rB_s) layers by E. M. Tanguep Njiokep, M. Salamon and H. Mehrer (Defect and Diffusion Forum, 2001, v.194-199, p.1581) were used. At 400°C, the parabolic constant k is reported to be 1.57×10^{-13} m^2 s^{-1} for the former compound and 1.63×10^{-14} m^2 s^{-1} for the latter. From these, smoothed layer thickness-time dependences were calculated. Then, the data thus obtained were treated using the system of equations 1. The values of k_A and k_B were found to be 3.40×10^{-13} m^2 s^{-1} and 9.37×10^{-14} m^2 s^{-1}, respectively. These remain unchanged in the 1.0×10^5-2.6×10^6 s time range. The constants k_A and k_B were also calculated using tabulated values of layer thickness against time in that range. Those were read from a graph. The derivatives were found by the numerical three-point method. The average value of k_A was determined to be 4.49×10^{-13} m^2 s^{-1} and that of k_B 9.41×10^{-14} m^2 s^{-1}. Both sets of the constants are seen to agree fairly well, providing evidence for the validity of the treatment proposed.

Kinetics of Growth and Lateral Spreading of a Spinel Layer Around NiO Particles on Al_2O_3

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The kinetics of thickening and lateral spreading of a thin layer of aluminate spinel $NiAl_2O_4$ around solitary NiO particles located over a single crystalline substrate Al_2O_3 have been analyzed theoretically and studied experimentally by SEM and AFM in the temperature range 1000 –1100°C. It was assumed that due to small layer thickness of the forming layer, the kinetics of thickening is limited by the reaction rate at the spinel-substrate interface, whereas the lateral propagation of the layer is controlled by surface diffusion. The rate of reaction at the spreading front of growing compound layer was also taken into account. By comparing the rates of lateral spreading with theoretical predictions, the diffusion coefficients of NiO associates on the spinel $NiAl_2O_4$ surface and the surface diffusion activation energy have been estimated.

Growth Kinetics and Silicon Diffusivity in $MoSi_2$ and WSi_2 Disilicides

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Growth kinetics and silicon diffusivities in $MoSi_2$ and WSi_2 silicide phases were studied at selected temperatures over the temperature range from 900 to 1500°C using reaction between dense metal and silicon vapor.

Experiments were carried out by electrothermography method [1] using molybdenum and tungsten wires 100 μm in diameter and 8.5 cm length as initial samples directly heated by electrical current. As a silicon source rarefied monosilane was used providing controllable conditions of the silicon supply to the metal surface. To ensure diffusive mode of interaction the partial pressure of silane was selected in the way that certain prevailing of the rate of silicon supply to the surface over the rate of its diffusion into the formed silicide layer was provided in order to hinder the formation of a redundant solid silicon layer (at $T < T_{melt}^{Si}$).

It is established that for the case of molybdenum two compact uniform layers ($MoSi_2$ and Mo_5Si_3) were observed in diffusion zone, and the $MoSi_2$ layer was by about one order of magnitude larger in thickness than the Mo_5Si_3 layer. In the case of tungsten a single-layered diffusive zone is formed, consisting of WSi_2 compact and uniform layer; the W_5Si_3 silicide is not detected at all. In all cases growth kinetics of disilicide layers, up to 5-7 μm thicknesses, conforms well to the parabolic law, which testifies indirectly that the first type boundary condition is realized on the gas medium/$MeSi_2$ boundary. The silicon diffusion coefficients in $MoSi_2$ and WSi_2 layers were calculated on the basis of measured parabolic growth constants.

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Diffusion Annealing of Mo/$MoSi_2$ Couple and Silicon Diffusivity in Mo_5Si_3 Layer

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Growth rate constants and silicon diffusivity in intermediate Mo_5Si_3 silicide layer were determined at temperature range from 1180 to 1800°C using Mo/$MoSi_2$ diffusion couple.

Experiments were carried out by electrothermography method [1]. Molybdenum wires 100 μm in diameter with preliminarily formed disilicide coating have served as initial samples directly heated by electrical current.

Due to application of a new preparation technique for initial Mo/$MoSi_2$ diffusion couple it became possible to widen essentially the temperature interval of kinetic measurements in comparison with our earlier investigation [2].

It was established that annealing those samples in inert medium led to diffusion transformation of the $MoSi_2$ into Mo_5Si_3 compact uniform layer while Mo_3Si silicide was not detected in the diffusion zone up to complete consumption of $MoSi_2$ layer. The growth kinetics of intermediate silicide layer followed to the parabolic law.

Experiments were supplemented with calculations of behaviour of the diffusion couple under study with and without taking into account the existance of the lowest silicide (Mo_3Si) thin layer.

Silicon diffusion coefficients in Mo_5Si_3 layer were calculated based on parabolic growth constants and using the approach described elsewhere [2].

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Reaction Diffusion in Mo-Si System Above the Melting Point of Silicon

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The results of direct kinetic measurements and SEM observations on formation of silicide phases in Mo-Si system at temperatures 1400-1700°C are presented in the work.

It is established that a multilayer diffusive zone is formed on the molybdenum surface when it comes in contact with molten silicon, and simultaneously, the metal is dissolved in liquid silicon with formation of Si-$MoSi_2$ eutectic. As a consequence of diffusive processes occurring in opposite directions, the boundary between silicide diffusion zone and eutectic melt can move in different directions depending on the ratio of Si and Mo fluxes.

As shown by means of SEM investigations of quenched samples, the primary product observed is disilicide phase, which is formed in the bulk of liquid silicon as fine particles with characteristic size less than 1 μm. After the melt is satiated by disilicide, the process of $MoSi_2$ crystallites nucleation and their growth takes place. The latter proceeds up to complete consumption of silicon after which the whole silicide zone becomes compact and includes two disilicede layers as well as a thin intermediate Mo_5Si_3 layer.

Thus, the formation of $MoSi_2$ final product proceeds by two various mechanisms. Accordingly, two types of final product microstructures are formed: (i) a compact layer (usually with expressed columnar structure) by the reaction diffusion mechanism; and (ii) separated fine grains by crystallization in the volume of saturated Me-Si melt.

A proposed model of product formation allows to calculate the relative contributions of the two above-listed mechanisms of disilicide phase formation at various stages of interaction and to estimate the role of each of them in the total process.

Reactive Diffusion and Kinetics of Niobium Carburization in Methane

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Reactive diffusion and growth kinetics of carbide layers in niobium-carbon system were investigated by means of heating niobium metal in carbon containing gaseous atmosphere at selected temperatures over the temperature range from 1400°C to 2300°C and reaction times from 0.1 s to 100 s.

Experiments were carried out by electrothermography method at strongly isothermal conditions. Thin niobium wires 100 μm in diameter and 8.5 cm length were used as initial samples, which were heated directly by electrical current. As a source of carbon, pure methane was used over the pressure interval from 5 to 300 Torr providing controllable conditions of carbon supply to the metal surface.

It is established that at comparatively lower methane pressures (up to 20-30 Torr), two carbide layers (Nb_2C and NbC) are formed simultaneously, the growth rates of which do not depend on methane pressure and fulfill the parabolic low. Over the methane pressure range 150-300 Torr practically at the beginning of the process alongside with carbide layers a pyrographite layer appears on the metal surface resulting in sharp decrease of the carbide layer growth. It was also shown that changing the interaction scheme from solid +gas to the solid +solid one, transformation of the diffusion zone structure takes place: the thickness of the outer carbide layer (NbC) decreases to a greater extent than the same for the inner layer (Nb_2C). As a result, the ratio of carbide layers thicknesses varies in time and increases tending asymptotically to the certain value.

The parabolic rate constants were measured and on their basis diffusion coefficients were determined in Nb_2C and NbC layers over the above-mentioned temperature range.

Vacancy Formation and Annihilation areas in Ti/Al and Ti/TiAl$_3$ Multiphase diffusion couples

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It has been well known that interdiffusion coefficient, D_i, determined by using single phase diffusion couples (S-couple) often differs from that determined by using multi-phase diffusion couples (M-couple). As the reason for the difference in the interdiffusion coefficients, some factors have been proposed. One is an effect of grain boundary diffusion. The other is the so-called phase boundary effect. In M-couples, many vacancies are generated or annihilated at phase boundaries due to discontinuous change in magnitude of vacancy flow. It has been considered that excess or deficient vacancies near the phase boundary sometimes enhance or retard diffusion near phase boundary as well as even at a distant place from the boundary. It is most likely that the place where interdiffusion might be enhanced is a vacancy annihilation area and it is never a vacancy formation area.

Both interdiffusion coefficients in Ti$_3$Al and TiAl determined from S-couples are more than one order of magnitude smaller than the interdiffusion coefficients determined from M-couples. As long as the interdiffusion in these diffusion phase layers is enhanced due to phase boundary effect, vacancies must be annihilated in these layers. When vacancies are formed in these phases, it should be concluded that the phase boundary effect is not a determinant factor that enhances interdiffusion in these phases.

In this work, vacancy formation or annihilation areas in Ti/TiAl and Ti/TiAl$_3$ M-couples have been clarified with the aid of the previous studies on Kirkendall effect and self-diffusion coefficients in Ti$_3$Al, TiAl.

Growth Kinetics of the $NiSi_2$ Spherical Inclusions in the NiSi Thin Film System

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Approximate solutions of initial boundary-value problem for the second equation of the Fick’s law in the framework of the diffusion model of the growth of spherical inclusions of the new γ-phase in the supersaturated α-solid solution were obtained. It is essentially to note that in the proposed model the particles of the new phase grow in somewhat limited region, not in the unlimited medium of the solid solution.

The elaborated algoritm of the numerical realization of the diffusion problem allows to simulate concentration distribution of the superfluous component, to presume the size of the inclusions, rate of their growth, time of the maximum size attainment. The following parametrs are varied: the initial concentration of diffusion substance C_o in the solid solution, the equilibrium concentrations of the diffusion substance in the matrix C_α and in the new phase C_γ, diffusion coefficient D and radius of the diffusion region R.

The model calculations were carried out for the case of the formation of the particles of the $NiSi_2$ silicide phase in the thin film system Ni(24nm)/Si. The growth kinetics of the radius of the spherical inclusion of the new phase and redistribution of the Si concentration on the different stages of the diffusion were considered.

Satisfactory accordance of the theoretical and experimental results was obtained, the Si diffusion coefficients for different annealing temperatures were determined. For example, the maximum radius of the $NiSi_2$ inclusion after annealing at 950^oC for 30 s is $2{,}3\cdot10^{-5}$ sm and Si coefficient diffusion is $6{,}9\cdot10^{-11}sm^2/s$.

Surface Pattern Formation During Interdiffusion and Surface Reaction in the Au/GaAs System

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The heat treatments performed during the metallization of GaAs results in a complex sequence of diffusion induced transformations. During the process, the continuity of the Au film breaks down, and islands with a wide size distribution are formed. The reaction at the Au GaAs interface is coupled with the partial decomposition of the GaAs matrix, formation of liquid phase eutectic alloy, and the release of As in the gas phase. In order to understand the sequence of reactions in this system, one must consider the interaction of gas, liquid and solid phases simultaneously.

We have preformed a set of experiments in closed and open gas phase systems and analyzed the resulting morphologies and phases. Cross sectional TEM analysis was performed simultaneously with the study of surface morphologies using SEM, AFM and optical microscopy. In this system, it is not possible to describe the diffusion process with the usual one dimensional model, which assumes the homogeneity of the sample perpendicular to the diffusion front. We made an attempt to identify the mechanism for the breakdown of the horizontal symmetry trough fluctuations. The enhancement of horizontal fluctuations eventually leads to the formation of the observed fractal patterns.

Destruction Kinetics of Organic Super Toxic Compounds. Diffusion Stage

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The problem of the conversion of organic super toxic compounds is the most important problem of the 21-th century. During the 20-th century the great number of toxic compounds was synthesized. Among them the pesticides and military phosphor organic compounds are the most dangerous. The ecological situation in the world needs the destruction of the stocks of all toxic substances in a short time.

The thermodynamic estimation shows that the complex organic compounds are not stable at high temperatures. More of them destroy by heating on 500 – 700^0C. Thereby for the destruction of super toxic substances one can use the thermo destruction process. The destruction degree is defined not only by equilibrium parameters but by kinetics of the process too. Therefore, the diffusion stage of the destruction process of some organic toxic compounds and it's effect on the rate of the whole process is proposed in the presented report.

Modeling of Oxidation of Fe-Ni-Cr Alloys

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We present the model of selective and competitive oxidation of multicomponent non ideal alloys. The model is based on;

- the generalized Darken method of interdiffusion;
- the Wagner model of the Ni-Pt alloy oxidation;
- the postulate that the values of fluxes in reacting alloy are limited (the kinetic constraint) and
- the thermodynamics of the Fe-Ni-Cr system.

We start from the initial stages of the reaction (non-stationary period of the reaction) during which the Cr surface concentration is time dependent, through the quasi-stationary period (constant Cr surface concentration in the alloy) up to complete chromium depletion from the oxidized alloy.

The model enables to predict the evolution of component distributions in the reacting ternary alloy. The results of the oxidation of the 310SS steel are presented and calculated concentration profiles are compared with the experimental data. The satisfactory agreement allows conclude that the oxidation reaction is limited by interdiffusion in reacting alloy. We compute the chromium depletion during the long term oxidation. The computations demonstrate that the chromium depletion is the key factor affecting the scale composition.

Prediction of the Depletion Zone Due to the Selective Oxidation of the P91 Steel

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We use the model of selective and competitive oxidation of multi-component alloys. The model bases on the generalized Darken method of interdiffusion in multi-component solid solutions and reactive diffusion in the growing scale. To avoid the nonphysical values of fluxes in reacting alloy we introduce the kinetic constraint on all fluxes. This method known as “flux limitation” avoids numerical non-stabilities, speeds up the computation time and gives good agreement with experimental results.

The results of the selective oxidation of the P91 steel are presented. Calculated concentration profiles are compared with the experimental data. The satisfactory agreement allows conclude that the oxidation reaction is limited by interdiffusion in reacting alloy.

We show the evolution of chromium distribution in oxidizing steel up to 100 000 hours. The computations demonstrate that chromium concentration in the steel at P91/scale interface is the key factor determining the scale composition.

Growth Mechanism of the Scale on Fe18Cr5Al Foil Preoxidised in SO_2 + 1 % O_2 Mixture

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It is believed that the unstable and stable aluminas grow via different mechanisms: the former due to the outward aluminium transport, while the latter due to the inward oxygen transport via oxide grain boundaries.

The two-stage oxidation method enables distinguishing two mentioned above mechanisms. It comprises sequential exposure in atmospheres containing highly different amounts of the $^{18}O_2$ tracer.

In this paper the results of the study of the scale growth mechanism on the Fe18Cr5Al 50 μm thick foil are reported. The experiments were carried out at 820 °C in two stages. In the first one, the samples were exposed to the SO_2 + 1 vol. % O_2 mixture for 1.5 and 24 h in order to produce the primary scale. The morphology of the scale is well developed and consist whiskers and pyramids structure. Subsequently, the samples were cooled down to the room temperature. Then, they were moved to the furnace where they were exposed to the atmosphere rich in $^{18}O_2$. During the second stage, they were oxidized for 0.5 and 4.5 h, and 8 h and 72 h, for both types of samples, respectively.

The elemental distribution was determined using high resolution SIMS, while the scale morphology was observed by means of SEM.

The results were interpreted in terms of the diffusion processes in the oxide scale.

Comparison of Two Methods of Calculation of Activation Energy for Selected Industrial Steels after its Oxidation at High-Temperatures in Air

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In this work it will be presented the results of calculation of energy activation *Q* of selected industrial steels (e.g. grade 55 - carbon steel, 4H14N14W2M and 50H21G9N4 valve steels) according to Polish Norm by two methods. In the first method the calculations of *Q* are based on the dependence of value of parabolic oxidation constants k_p in function of reciprocal temperature. The second method is based on the calculated parameters, which allow to determine the value of *Q* for examined steels by using value of *Q* for pure iron, taken from literature data, and the particular values of mass concentrations of elements in oxidised steels. The growth kinetics of layers were close to parabolic law. The values of parabolic oxidation constants k_p were determined on the ground of measurements of thickness of oxidised layers. To the experiment the cylindrical specimens were used. The isothermal process of oxidation was conducted in chamber furnace at 1100, 1060, 1020, 980 and 940°C in the air. Time of oxidation various from 3 till 117 hrs. The comparison of obtained results of activation energy *Q* for mentioned methods of individual examined steels gives a good agreement.

Lifetime Estimation for MCrAlY Coatings on Industrial Gas Turbine Blades Based on Diffusion-controlled Processes Moddelling

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MCrAlY – type coatings are used world-wide in modern stationary gas turbines for electric power generation as protective overlay coatings against oxidation (M comprises Ni and/or Co). The life time of the MCrAlY coatings is diffusion and oxidation controlled process and constitutes about 30000 h (~3-4 years) and more. Experimental investigation of the diffusion process is in general very costly and time-consuming. The conventional calculational approaches are usually too complex for an application in industrial practice due to lacking model parameters (Al diffusion coefficients for coating-base alloy system for instance), especially for the multicomponent alloys used in modern coatings and blades (5 and more elements). Due to this fact the models are not adequate to treat real physical processes and they cannot yield the coating life time with the required accuracy. An analytical and experimental approach using inverse problem solution was developed . This approach is based on the models that describe the main diffusion and oxidation processes within the coating-base metal system. The model adequacy to physical processes is provided by identifying model parameters with short-time-experiment data for coating–base alloy systems. The model, theoretical and experimental approach as well as MCrAlY life time estimation results for 10000 h at 950°C are presented. These results were obtained with short time experimental data for Al concentration profiles across the coating thickness measured after 300 and 1000 h and confirmed by long term exposure.

Duration of Volcanic Processes and Implications for Assessment of Volcanic Hazards from Diffusion Modeling Studies

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Silicate minerals found in volcanic rocks preserve compositional gradients of major (= stoichiometric constituents) and trace (= dopants) elements, indicating that high temperature (~ 800 – 1200 °C) processes responsible for volcanic eruptions did not last long enough for chemical equilibrium to be obtained. Consequently, knowing diffusion coefficients of these elements and using techniques of diffusion modeling, the duration of such processes can be determined. Our results indicate that the processes occur entirely within the range of historical time scales of interest for development and planning of human settlements and consequently, may play a key role in societal issues such as mitigation of volcanic hazards.

We have performed diffusion modeling of chemical gradients found in two silicate minerals from volcanic rocks - plagioclase ($NaAlSi_3O_8$-$CaAl_2Si_2O_8$), the most abundant silicate mineral on the earth's crust, and olivine (Mg_2SiO_4-Fe_2SiO_4). For diffusion of elements found in low concentrations (parts per million) in plagioclase we find that it is necessary to consider the coupling between trace elements and the major stoichiometric constituents to properly describe the diffusion process. For modelling diffusion in olivine, it is necessary to consider the anisotropy of diffusion. The theoretical developments and numerical models developed for these problems can be generally adapted to a wide class of problems and materials.

The models were applied to lavas from Volcan San Pedro (Chilean Andes 36º S). The results indicate that the time that the rocks remained at high temperatures below the volcano before eruption is in the order of months to ~100 years. Such timescales can only be retrieved by kinetic modeling and should contribute to forecasting of volcanic eruptions.

Sedimentation of Atoms in Se-Te Solid Solution under an Ultra-Strong Gravitational Field

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The ultra-strong gravitational field experiment was performed on the all-proportion miscible $Se_{70}Te_{30}$ semiconductor by a new ultracentrifuge apparatus in JAERI. The specimen was treated under an ultra-strong gravitational field of 1,020,000 G in maximum acceleration for 100 hours at a temperature of 260^0C, which was below the melting temperature of about 280^0C. As a result, the Te content increased in the direction of gravity from about 0 to 60 at.%, while the Se content decreased from about 100 to 40 at.%. The lattice constants of the hexagonal structure continuously increased with increasing the gravitational field. The change in the lattice parameters exactly showed that the graded structure was formed on the atomic scale. This also showed that the sedimentation of substitutional solute atoms occurred in this solid solution. In the graded structure region, the crystal growth along the direction of gravity was observed. The simulation result of the sedimentation process showed that the diffusion coefficient of sedimentation was larger than that of normal diffusion due to the internal chemical potential by more than 10 times.

Faceting of Σ3 grain boundaries in Cu: three-dimensional Wulff diagrams

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The faceting of cylindric tilt grain boundary in Cu bicrystal containing full spectrum of inclinations has been studied at 0.95 of melting temperature T_m. Both grains form the superlattice called coincidence site lattice (CSL) with Σ=3. The $(100)_{\mathrm{CSL}}$ facet and non-CSL 82°9*R* facet are observed. The ratio between GB energy σ_{GB} and surface energy σ_{sur} was measured by atomic force microscopy using the GB thermal groove method. The influence of misorientation deviation $\Delta\theta = |\theta - \theta_\Sigma|$ from coincidence misorientation θ_Σ has been studied. The 3-dimensional Wulff-Herring diagrams were constructed using measured $\sigma_{GB} / \sigma_{sur}$ values. They reveal that only $(100)_{\mathrm{CSL}}$ and 9*R* facets correspond to the energy minimum at low $\Delta\theta$. No rough edges between $(100)_{\mathrm{CSL}}$ and 9*R* facets were observed. It means that T_m is lower than the roughening temperature for these facets in Cu. By increase of $\Delta\theta$ the energy of $(100)_{\mathrm{CSL}}$ facet increases. The financial support of Russian Foundation for Basic Research, German Federal Ministry for Education and Research, Deutsche Forschungsgemeinschaft, NATO and INTAS is acknowledged.

Ab initio calculation of vacancy formation and migration energies in FCC metals: LDA versus GGA

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We have investigated the effect of the choice of the exchange-correlation functional in ab initio calculations of vacancy formation and migration energies, E_f and E_m, in FCC transition and noble metals (Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au). The calculations are performed using a plane-wave pseudotential approach, implemented in the PWSCF code, and supercells of 64(-1) atoms with a relaxation of the atomic positions. Two sets of results are obtained using either the Local Density Approximation (LDA) or the Perdew-Burke-Ernzehof (PBE) formulation of the Generalized Gradient Approximation (GGA).

We find that for E_f the GGA values are lower by 0.25 ± 0.05 eV than the LDA ones and that for E_m they are 10% lower. These results are consistent with recent calculations using similar approaches or all electron methods [1,2]. Both functionals yield the same unexpected results concerning the relaxation pattern around the vacancy. The relaxation amplitudes and energies are found to be not negligible in *4d* and *5d* metals, at variance with empirical potential calculations. We discuss the possible origin of this electronic-structure effect.

Concerning the comparison with available experimental data, the experimental values of E_m lie in between the LDA and GGA values, whereas for E_f the calculated values are found to be always overestimated. For E_f the discrepancy with experiments is larger for GGA than for LDA, and it increases when going from *3d* to *4d* and *5d* elements.

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Which is larger, a Self-Interstitial or a Vacancy Activation Energy of Diffusion in Silicon?

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The processes related to thermal oxidation of silicon crystal surface and to a dopant diffusion in the crystal are indispensable for the silicon semiconductor device fabrication. The thermal oxidation of the silicon surface generates extrinsic stacking faults. This indicates that self-interstitials generated at the Si/SiO_2 interface diffuse into the bulk inside. And self-interstitials are still in the supersaturated state although they are captured by vacancies in the bulk, while vacancies are in the undersaturated state. Diffusions of substitutional impurities such as P, B and As in silicon are enhanced by the thermal oxidation. On the other hand, it is found that the diffusion of Sb atom is retarded. This indicates that substitutional atoms in silicon diffuse via both self-interstitials and vacancies in silicon. Grown-in defects in silicon crystal cause a serious problem resulting from the trend toward small scale and highly integrated circuits used in semiconductor devices. There is no doubt that intrinsic point defects are closely related to the formation mechanisms of these defects. Understanding of behavior of the point defects is thus extremely important. Although a large number of papers relevant to intrinsic point defects have been reported, we cannot well understand them yet. We conclude that the activation energy of a self-interstitial is larger than that of a vacancy according to experimental results of dopant diffusions. That is, $\partial_T \ln[D_V] < \partial_T \ln[D_I]$ $(\partial_T \equiv \partial / \partial T)$ are derived for an arbitrary absolute temperature T. This relation is a necessary condition for the obtained results of diffusivities of self-interstitials and vacancies in this field.

Study of Fe Diffusion in Cr_2O_3 by Secondary Ion Mass Spectrometry

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Cr_2O_3 layers grown by thermal oxidation on stainless steels are effective to protect these alloys against corrosion by oxidation at high temperatures. In order to check if these Cr_2O_3 layers play the role of a diffusion-barrier for Fe from metallic substrates in those alloys, Fe diffusion has been investigated in high density polycrystalline Cr_2O_3, obtained by hot pressing, and in Cr_2O_3 layers grown on Ni-30%Cr alloy. A film of Fe was deposited on the surface of either polished polycrystalline Cr_2O_3 or on the outer surface of the Cr_2O_3 layers on Ni/Cr. Then the iron film was oxidized in pure oxygen at low temperature for short time before diffusion annealing. The diffusion experiments were performed from 720^o C to 1100^o C, under oxygen partial pressure of 10Pa. The Fe diffusion profiles were determined by secondary ion mass spectrometry (SIMS). The experiments led to the determination of Fe effective diffusion coefficients (D_{eff}), determined in the first part of the diffusion profile, using a solution of Fick's second law for diffusion from a thick-film. Le Claire's model was used to determine the product $D_{gb}\delta$ from the tail of the diffusion profiles, where D_{gb} is the grain-boundary diffusion coefficient and δ is the grain-boundary width. Hart's equation allowed to obtain both the bulk and the grain boundary diffusion coefficients. The dependence of these diffusion coefficients on temperature are described by means of Arrhenius' equations. Analysis of the results obtained in polycrystalline Cr_2O_3 and in Cr_2O_3 layers show that the microstructure of the material strongly affects the diffusivity of the iron. Comparison of iron diffusion with chromium self-diffusion in Cr_2O_3 shows that iron diffuses slightly slowly than chromium.

Faceting of Σ3 grain boundaries in Al

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Faceting can be considered as a phase transition when the original surface or GB dissociates onto flat segments whose energy is less than that of the original surface or GB. GB faceting can strongly influence the diffusion permeability of polycrystals and other diffusion-controlled phenomena like grain growth. GB faceting proceeds only close to the so-called coincidence misorientations. In this case the lattices of both grains form the coincidence site lattice (CSL) characterized by the parameter Σ (reverse density of coincidence sites). For the investigation of GB faceting an Al bicrystal with an semi-island grain was grown with the aid of the modified Bridgman technique. Grain *1* in this bicrystal is semi-surrounded by grain *2* forming the Σ3 <110>tilt GB. The faceting was analyzed in an *as-grown* bicrystal and after annealing at 600, 550, 500, and 450°C. Main facet is the symmetric Σ3 twin ($\{111\}_1/\{111\}_2$ or $(100)_{\Sigma3CSL}$ facet). The second facet form an angle of 82° with the $\{111\}_1/\{111\}_2$ or $(100)_{\Sigma3CSL}$ sides. The studies in Cu revealed that this 82° facet has a so-called 9*R* structure forming a plate of body-centred cubic GB phase in the face-centred cubic matrix. Third facet is the $(110)_{\Sigma3CSL}$ one. The bicystalline samples were coated with a layer of Zn-Al mixture and annealed in the two-phase area of the Al–Zn where the solid (Al) phase is in equilibrium with (Zn) melt. The contact angles were measured after quenching and sectioning on the ground and polished surface. Respective Wulff-Herring plots were constructed.

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An Analysis of the Effective Diffusivity in Three-Phase Composite Material Consisting of the Host and Coated Inclusions

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In this paper, we discuss first the problem of determining and analyzing the effective diffusivity in composite materials. We focus on the problem of determining the effective diffusivity of a three-phase material consisting of a host phase, inclusions and a coating phase on the inclusions, with all three phases exhibiting different diffusivities. Extending and adapting the formalism derived originally by Maxwell for a two-phase system we arrive at a closed form expression for the effective diffusivity for the three-phase material. We also show how to extend the analysis to the case where the inclusions have different sizes and the coating phase is assumed to have a constant width. The derived expression for the effective diffusivity is tested on some simple models for the material using a fine-grained Monte Carlo random walk method. It is shown that the derived expression is considerably superior to other descriptions of the effective diffusivity for the combinations of diffusivities chosen. It is also suggested how to use the derived expression as a basis for building numerical algorithm for the case when the sizes of the inclusions can be described by statistical methods.

Coupling Effect in Diffusion of Carbon Atoms in the Cottrell Atmospheres

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Diffusion of carbon atoms in the Cottrell atmospheres in ultra-high purity Fe-C alloys can be successfully analyzed by low-frequency mechanical spectroscopy. Existence of the coupling effect, that is, cooperative diffusion of carbon atoms (carbon atoms interact with each other as well as with the dislocation) is deduced from experimental studies [1, 2] and computer simulations [3]. The relaxation process responsible for the so-called Snoek-Köster relaxation is recognized as a complex many-body correlated interaction process. This approach is exemplified by several theoretical considerations and new experimental data. Comparison between computer simulations and experimental results obtained in deformed Fe-C alloys is discussed.

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Influence of Composition on Diffusion in Nickel Aluminides

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Original results on ^{67}Ga and ^{68}Ge diffusion in Ni-rich Ni_3Al alloys are reported in this paper. The measurements were carried out in the temperature range from 773 to 1173 K using the residual activity method. The concentration dependence of the ^{67}Ga volume and grain boundary (GB) diffusion was studied for three compositions between 22.4 and 24.8 at.% Al in pure (not boron alloyed) Ni_3Al alloys. In the case of ^{68}Ge diffusion, the volume diffusion in pure Ni and GB diffusion in Ni-24.8Al were studied.

Similar to literature data on the ^{63}Ni GB diffusivity in Ni_3Al, ^{67}Ga GB diffusivity in nickel-rich Ni_3Al, in the present paper increased with increasing Ni concentration. Observed values of activation energy were higher and GB diffusivities were lower for alloy with maximum Ni content compared to respective values for ^{67}Ga GB diffusion in nickel.

GB diffusivities of ^{68}Ge in Ni_3Al were higher than those of ^{67}Ga and the activation enthalpy was lower, which agree well with the expected differences in segregation behavior of both the elements.

The results were compared with the literature data on self-diffusion in nickel aluminides and were interpreted in terms of bulk and GB composition. It seems that – for the volume diffusion – the Ga, the Ge and partially also the In simulate reasonably the Al self-diffusion in Ni_3Al, but this is not so unambiguous in the case of the GB diffusion in Ni_3Al. It is argued that the reason may consist in significant differences in segregation behavior of these elements to GB's.

Jump Frequency of Cd Tracer Atoms in β-Mn

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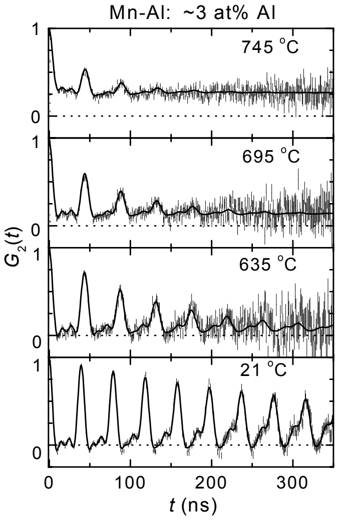
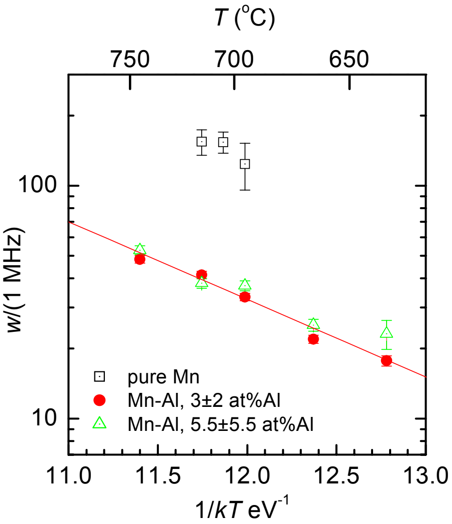
Diffusion has not been measured previously in β-Mn, which is stable between 655-1080° C and has a 20-atom unit cell with two inequivalent sublattices. De Doncker et al. showed for quenched β-Mn using perturbed angular correlation (PAC) that ^{111}In/Cd tracer atoms occupy the 12d sites and have a large electric field gradient (EFG). PAC measurements have been made by us at high temperature for pure β-Mn and alloys containing Al. Spectra exhibit nuclear quadrupole relaxation attributed to Cd atoms jumping among sites of the 12d sublattice (left figure). Each 12d atom has six 12d neighbors at distances of 0.26 nm, and the efg reorients by roughly 70° in each jump. Spectra were fitted to obtain jump frequencies w using the approximate relaxation model of Baudry and Boyer. At right are shown fitted jump frequencies, with the line corresponding to activation enthalpy 0.77(3) eV and prefactor 3.2(1)x 10^{11} Hz. w is seen to be four times larger in pure β-Mn than in the alloys. The relationship between jump frequency and diffusivity will be discussed.





Ru Self-Diffusion and Ru Diffusion in Al

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Experimental measurements of Ru self-diffusion in the range of temperature (1173-1473) K and Ru diffusion in pure Al in the range 632-913 K will be presented. The ^{103}Ru radiotracer was used for self- and hetero-diffusion studies. In the last case, the Heavy Ions Rutherford Backscattering Spectroscopy (HIRBS) technique was used for measuring the diffusion coefficients at low temperatures. The results obtained are discussed as well as the difficulties found when working with pure Ru.

This work is the first step in a program of diffusion studies in the RuAl compound. Ordered intermetallic compounds are the subject of extensive research in connection with their potential applications as high-temperature structural materials. The stiffness of intermetallics are often greater than those of the metals from which they were formed and they frequently maintain their strength better with increasing temperature than do disordered alloys. The low specific density of many of them produce high specific stiffness and specific strength, quantities that are vital to uses in aircraft, spacecraft, and rotating parts. There are two awkward aspects of intermetallics for high-temperature use: many oxidize rapidly at proposed temperatures of use and virtually all are brittle at ambient temperature; either of these behaviors is sufficient to disqualify a material.

Unlike most structural intermetallics, RuAl is found to combine a very high melting point (≈ 2060 °C), high-temperature strength and oxidation resistance with useful room-temperature toughness. It is highly resistant to environmental degradation in some very severe chemical media and impervious to attack in most hot mineral acids. Diffusion data will be necessary to understand material transport in RuAl matrix.

Interdiffusion Studies in Co-Fe-Ni Alloys

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Interdiffusion in Co-Fe-Ni alloys was studied in 1373-1588 K temperature range. The Darken Method for multi-component systems (GDM) was used for the description of the interdiffusion process in ternary Co-Fe-Ni diffusion couples both for the finite and infinite geometry. Using the inverse method (based on GDM), the average intrinsic diffusivities of components in the Co-Fe-Ni system were calculated and compared with the results of the other authors. The activation energies of cobalt, iron and nickel have been found in 1373-1588 K temperature range.

Sr Diffusion in La-doped $SrTiO_3$ under Oxidizing Conditions

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On $SrTiO_3$(100) and (110) single crystals doped with 0.02 or 1 at.% La tracer diffusion experiments were carried out in synthetic air at temperatures of 1300 to 1500 °C. After equilibration annealing, the typical growth of SrO_x islands is observed. The coverage increases with the La content supporting the model [1] that on oxidation the donor is compensated by Sr vacancies. The tracer sources were applied by two different methods: (a) ion implantation of $^{87}Sr^+$, and (b) chemical solution deposition of a polycrystalline $^{86}SrTiO_3$ layer. The depth profiles were measured by secondary ion mass spectrometry (SIMS). The Sr tracer diffusivity is found to be several orders of magnitude lower compared to O, La and Nd. It increases strongly with the dopant concentration, indicating a cation vacancy mediated transport. At high dopant concentration, the Sr diffusivity is close to the Ti diffusivity reported recently [2], suggesting a similar diffusion mechanism. Although microscopic and spectroscopic investigations of the samples yielded a strong dependence of the surface reconstruction on the crystal orientation (see [3] and refs. therein), the bulk diffusivity is isotropic as expected for a cubic crystal.

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Diffusion of Hydrogen in Amorphous Ceramics in the System Si-(B)-C-N

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None-oxide ceramics in the system Si-(B)-C-N have potential applications as high temperature materials and as wide band gap semiconductors. These precursor derived ceramics with thermolysis temperatures up to 1400 °C are amorphous and contain in addition to the constituting elements Si, N, C and B about 6 at. % of hydrogen. Thermal treatment in nitrogen at temperatures above the thermolysis temperature leads to structural changes indicated by a loss of hydrogen to less than 1 % and the beginning of crystallization. Hydrogen diffusion plays an important role in the investigation of the mobility and the kind of defects in the amorphous state as well as for the passivation of electronic defects. In this work we measured the diffusivities of hydrogen of Si-C-N and Si-B-C-N bulk ceramics using as-thermolyzed samples and samples pre-annealed at temperatures above the temperature of thermolysis. The deuterium tracer was introduced via gas exchange at temperatures between 700 °C and 1100 °C. Depth profiling was done with secondary ion mass spectrometry.

The deuterium profiles can be fitted with complementary error functions. The diffusion coefficients obey Arrhenius laws. For samples with different chemical compositions pre-annealed at 1460 °C a unique activation enthalpy of 2.1 eV and a pre-exponential factor of 10^{-8} m^2/s is observed, for samples pre-annealed at 1600 °C diffusion becomes faster. These data can be understood in the framework of a reaction limited diffusion mechanism: in the case of local equilibrium Fickian diffusion behaviour is observed with an effective diffusion coefficent, which depends on the concentration of traps.

Interdiffusion of Niobium (Columbium) and Molybdenum in Nickel between 900 – 1300 °C

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Niobium and Molybdenum are two important alloying elements found in nickel base superalloys. Both elements improve creep resistance by being strong solid solution strengtheners while Nb also acts as a precipitation hardener. Because of their significant role in superalloy metallurgy, there is a need to understand the diffusion behaviour of these elements in Ni. In case of Nb, diffusion data is virtually absent while for Mo, although considerable volume of data exist, there still is a requirement to establish diffusion coefficients more accurately.

In this work, the interdiffusion coefficients of Mo (D_{Mo}) and Nb (D_{Nb}) have been determined in the 900-1300°C temperature range using diffusion couples made between pure Ni with either Ni10wt%Mo or Ni4wt%Nb alloys. These were annealed at 900, 1000, 1100, 1200 and 1300°C for a number of time periods in Ar atmosphere. After annealing, concentration profiles of diffusing elements in each couple were obtained using EPMA.
These profiles, were then used to calculate D_{Mo} and D_{Nb} as a function of composition using the modified Boltzmann-Matano method. The extracted values for D_{Mo} were found to be in very good agreement with published results in literature. Up to 10 wt% Mo and 4wt% Nb, we found that there is very little concentration dependence in D_{Mo} and D_{Nb}. Both coefficients, however, show a strong Arrhenius type behaviour above 900°C as described by:
$D_{\mathrm{Mo}}\ (\mathrm{m^2/s}) = 1.2\ (+0.4 / -0.3) \times 10^{-4} \exp\{-281.3 \pm 3.7\ \mathrm{kJmol^{-1}} / \mathrm{R}T\}$
$D_{\mathrm{Nb}}\ (\mathrm{m^2/s}) = 8.8\ (+3.2 / -2.3) \times 10^{-5} \exp\{-257.0 \pm 3.6\ \mathrm{kJmol^{-1}} / \mathrm{R}T\}$
where R is the universal gas constant and T, absolute temperature. These results, together with others of ours published elsewhere, indicate that the transition metal Nb is one of the fastest diffusers in the superalloys.

Volume Diffusion and Magnetic State of Iron, Cobalt and Rhodium in Single Crystals of Iridium

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Volume diffusion coefficients of cobalt, iron and rhodium and parameters of the temperature dependence of the volume diffusion coefficient of cobalt in iridium single crystals have been measured using the secondary ion mass spectroscopy after their simultaneous diffusion under a ultra high vacuum at temperatures from 1540 to 1780 K (0.57 to 0.66 T_m). Parameters characterizing vacancy complexes of these atomic probes in iridium have been estimated. A conclusion has been drawn that vacancy complexes of Co, Fe and Rh possess stable local magnetic moments in iridium. The interaction energy of partners in these complexes has been estimated.

Implantation Fluence Effect on As Diffusion in Relaxed SiGe

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A systematic study of ion implanted As diffusion in relaxed $Si_{1-x}Ge_x$ has been performed as a function of implantation fluence. The compositions studied were x = 0, 0.2, 0.35 and 0.5 with implantation fluences of 5E8-4E14 cm^{-2}. Some of the samples were pre-annealed after implantation and all samples with the same composition were simultaneously isothermally diffusion annealed. The depth profiles were determined using the modified radiotracer [1] and Secondary Ion Mass Spectrometry (SIMS) techniques.
The results show that at low fluences 5E8-3E10 cm^{-2} no differences in the obtained diffusion coefficient values at a fixed temperature exist in case of the studied SiGe compositions. Comparison to the results of our earlier work [2] shows very good diffusion coefficient reproducibility and no effect of pre-annealing. With fluences 4E13-4E14 cm^{-2} pre-annealing decreases the As diffusivity as the implantation induced damage is partly annealed out, but it is still about 2-5 times higher than the As diffusivity observed with the low fluences. No differences in the results obtained by the radiotracer and SIMS profiling techniques for identical samples were observed. In case of pure silicon samples no fluence effect was observed.

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Interdiffusion in Fe/Pt Bulk Diffusion Couples

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An L1o ordered FePt phase is one of the most promising materials for ultrahigh-density magnetic recording media and for various micro-magnetic device applications as well as bulk permanent magnets because of its large magnetic anisotropy of 107-108 ergs/cm3. However, high temperature annealing above 773 K is indispensable for the formation of L1o ordered phase in multi-layer thin film, mono-layer thin film and bulk FePt. From a practical viewpoint, such high temperature annealing processes are unsuitable for mass productions of magnetic recording media, so it is necessary to lower the ordering temperature, which is related to the atomic diffusion. Annealing typically leads to combine reactions such as ordering, recrystallization, grain growth and sintering or coalescence concerning the elimination of crystalline defects such as dislocations, vacancies, grain boundaries and external surfaces. The combined transformation can be considered as two reactions occurring either simultaneously or sequentially. In case of simultaneous reactions, it is possible to substantially shorten the reaction times and lower the reaction temperature by helping the reaction each other. For further improvement of ultrahigh-density magnetic recording media, it is important to understand the ordering kinetics and its mechanisms including diffusion mechanisms. In order to clarify the ordering process of L1o FePt phase, it is needed to evaluate the activation energy of ordering and of atomic interdiffusion in FePt. In this study we report the experimental results of the interdiffusion and the reaction diffusion in Fe/Pt bulk couples. The diffusion coefficients and the activation energy for diffusion of Fe/Pt bulk couples will be compared to

that of Fe/Pt thin film couples.

Lanthanide Diffusion in Single Crystalline and Polycristalline Pure or Yttrium-doped Alpha-alumina.

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In order to bring a contribution to cationic diffusion in alpha-alumina, results on diffusion of 14 lanthanides and Sc and Y are presented. Samples are either single crystals with a known orientation or polycrystals with various grain-sizes elaborated from Y-doped alumina powders (100 ppm or 1000 ppm) or from nominally pure alumina powder. After pre-heating in air at the diffusion temperature small drops of a solution containing these elements are deposited at the surface of the sample. After the diffusion treatment (1200°C, 48h or 1300°C, 21h), the diffusion profiles are obtained by a CAMECA IMS 4F SIMS device. The isotopes which are taken into account are: ^{45}Sc, ^{89}Y, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{158}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{174}Yb and ^{175}Lu which are the most suitable for this analysis. At first, it can be observed that the diffusion profiles are quite similar for all the lanthanides, suggesting similar diffusion processes for all elements.

Diffusion profiles obtained for single crystals allow the calculation of the lattice diffusion coefficients, which are necessary to determine the diffusion coefficient values in grain boundaries.

Lattice and grain-boundary diffusion coefficient values are compared with cationic and oxygen self-diffusion coefficients determined earlier.

Non-destructive Methods of Diffusion Parameters Determination in Solid States

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The theoretical and experimental substantiation of new methods for diffusion parameters determination (diffusion coefficient and its concentration dependence) is carried out. For determination of the concentration dependence of diffusion factor by non-destructive method it is necessary to create an initial distribution of an impurity with a maximum at some depth of a sample and to define experimentally the time *t* of achievement of a surface concentration maximum. Thus accuracy of the diffusion parameters calculation will depend practically only on an uncertainty in *t* determination. This error will be much less, than in the case of usual methods as there is no necessity for the determination of absolute concentration value and depth of a layer.

The described technique was used during experimental research of subsurface diffusion characteristics of such ion-alloyed materials as: silicon alloyed by boron, and the tungsten single crystals alloyed by nitrogen. The initial impurity distribution and diffusion profiles for various annealing times were defined by secondary-ion mass-spectroscopy. Change of surface concentration was investigated by means of Auger electron spectroscopy. The structure of the investigated materials was controlled by means of optical microscopy and x-ray analysis.

The basic feature of the obtained results is the presence of several maxima on the time dependence of surface concentration of an impurity. The mathematical simulation has shown that this fact is explicable in terms of the existence of several impurity atom fluxes in subsurface areas of ion-alloyed materials with various diffusion constants.

Interdiffusion and Aluminum Self-diffusion in Iron-aluminides

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We have investigated interdiffusion in iron-aluminides using single-phase interdiffusion couples of Fe_xAl_{1-x}-Fe_yAl_{1-y} for three different aluminium contents between 18 and 50 at. %. Experimental diffusion profiles were obtained from electron microprobe analysis of the diffusion zone. Interdiffusion coefficients were deduced via the Sauer-Freise method taking into account volume changes. A temperature interval between 997 and 1447 K was covered in our experiments. Thermodynamic factors were deduced from a semiempirical model. The Darken-Manning equation was used to deduce self-diffusion coefficients of aluminium from the present interdiffusion coefficients, the calculated thermodynamic factors and the iron tracer diffusivities obtained by Eggersman and Mehrer (Phil. Mag. A 80 (2000) 1219). The results show that aluminium diffusion is always slightly faster than iron diffusion. The difference never exceeds a factor of two and indicates that iron and aluminium diffusion in iron-aluminides is closely coupled.

Tracer diffusion of Fe and Pd in FePt and $FePt_3$

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The ordered phases in the Fe–Pt system, FePt (tetragonal, $L1_0$) and $FePt_3$ (cubic, $L1_2$), are of interest as convenient model alloys for fundamental studies of phase equilibria and diffusion in fcc-based ordered alloys. In order to provide basic data of atomic diffusion, the tracer diffusion coefficients of Fe and Pd in these alloys have been measured by radiotracer experiments, following the measurements of chemical diffusion [1, 2]. In the ordered state, in both alloys the tracer diffusion coefficients are smaller than the chemical diffusion coefficient by a factor of 3 to 10, the extent depending on the composition and temperature. In the $L1_2$ ordered $FePt_3$, the diffusion of Pd is faster than Fe, suggesting that Pd atoms preferentially occupy the majority sublattice sites, substituting for Pt atoms. The experiments on the $L1_0$ ordered FePt have been performed using single-variant single crystal specimens prepared by heat-treatments under a compressive stress [1]. The diffusion of Fe measured on those specimens exhibits the expected anisotropy: the diffusivity is slightly but noticeably lower in the direction parallel to the tetragonal axis, which is perpendicular to the layered atomic arrangements. Effects of composition and order-disorder transition have also been examined and will be reported.

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"Up-Hill" Interdiffusion and Accompanying Effects in Ternary Cu-Ni-5 at. % Sn(In) Systems

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Experimental results and computer simulation of interdiffusion in couples composed of homogeneous alloys Cu-5 at. %.Sn - Ni-5 at. % Sn and Cu-5 at. %. In - Ni-5 at. % In have been presented and analyzed. The three-layered sandwiches Cu-5 at. % Sn(In)/ Ni-5 at. % Sn(In)/Cu-5 at. % Sn(In) with inert marks between the layers were used. The up-hill Sn(In) diffusion was detected after annealing (800°C) at the Ni-side of the ternary diffusion zone. Up-hill diffusion manifested itself in appearance of Sn(In) concentration peak near the interface of diffusion zone with Ni-5 at. % Sn(In) alloys. The maximum of Sn(In) concentration reached 10 at. %, i.e. became twice higher than initial Sn(In) concentrations in the constituent alloys. In the system Cu-Ni-5 at. % Sn precipitates of $(CuNi)_3Sn$ phase were nucleated in metastable ternary solution at the top of Sn concentration peak, and two-phase diffusion zone was developed.

By measuring the Kirkendall shifts and concentration profiles of each component in the ternary diffusion zone the partial diffusion coefficients and their concentration dependencies were calculated. These data were used for computer simulation. The concentration profiles obtained as a result of computer simulation fully reproduced the experimental ones. According to the results of computer simulation the redistribution of initially uniformly distributed Sn(In) atoms is caused by the gradient of chemical potential of Sn or In atoms in the Cu-Ni-5 at. % Sn(In) system. The calculated chemical potentials of Sn(In) atoms in Cu-alloys are higher than those in Ni-alloys that initiates Sn(In) diffusion to the Ni-side of diffusion zone. The appearance of Sn(In) non-homogeneity is caused by difference in diffusivities of the components. The criteria for formation of non-homogeneous diffusion zone during interdiffusion are formulated.

Ferromagnetic Influence on α-Fe Diffusion

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Diffusion of several no-magnetic impurities in α-Fe were studied in an extended temperature range, using Ion Beam techniques. In all cases, linear Arrhenius plots were obtained in the paramagnetic region, with a break at the Curie temperature (1043 K) and an up-ward curvature in the ferromagnetic region. This behaviour is explained in terms of a progressive lattice stiffness due to the progressive alignment of the magnetic spins, as in the self-diffusion case.

The maximum increment in the activation energy due to the ferromagnetic alignment (corresponding to 0 K) is almost the same for all the non-magnetic diffusers: around 40 kJ/mol as deduced from the experimental results. The conservation of that quantity is also theoretically calculated using the WIEN97 program, which is an implementation of the linearized augmented plane wave (FP-LAPW) method based on density functional theory.

In consequence, such kind of diffusers can be considered as “magnetic vacancies” in the ferromagnetic lattice, and the diffusion coefficient at low temperatures of other non-magnetic impurities can be easily extrapolated from the paramagnetic high temperature region.

Chemical Diffusion and Ionic Conduction in TiO_2

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Both single crystal and polycrystalline TiO_2 specimens were equilibrated at an ambient partial pressure $p(O_2)$ 10^0 -10^5 Pa over the temperature range 980-1390K. At those conditions the n- to p-type transition was observed. The determined values of the $p(O_2)$ exponent differ from those predicted by defect disorder models. This difference allows the evaluation of the ionic conductivity. On the other hand the kinetics of equilibration monitored by measuring electrical conductivity allows the determination of chemical diffusion coefficient. It was found that the ionic transfer number at the n-p transition regime is approximately 0.5. Basing on defect structure in TiO_2 the relationship between chemical diffusion coefficient and self diffusion coefficients of both titanium and oxygen was deducted.

Impurity Diffusion of ^{66}Ga in Relaxed Intrinsic $Si_{1-x}Ge_x$

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A study of ion implanted Ga diffusion in relaxed $Si_{1-x}Ge_x$ has been performed as a function of Ge content. The compositions studied were x = 0, 0.1, 0.15, 0.2, 0.25, 0.35, 0.5, 0.65, 0.8 and 1. The depth profiles were determined using the modified radiotracer technique [1] combined with the production of the radioactive ^{66}Ga ions employing the IGISOL (Ion Guide Isotope Separator On Line) technique at the University of Jyväskylä. All samples were annealed at 930 ^{o}C under argon atmosphere and the diffusion length was controlled by the annealing time. As the implantation fluences were only $5x10^7 – 5x10^8$ cm^{-2}, the effect of implantation induced damage to Ga diffusion was negligible [DIMAT poster (P. Laitinen)].

Gallium is known to diffuse via the vacancy mechanism in pure germanium and via the interstitial mechanism in pure silicon [2]. In $Si_{1-x}Ge_x$ vacancy mechanism has been found to dominate Si and Ge self-diffusion [3,4] as well as the diffusion of As [5], when $x > 0.35$. As a function of x ($x > 0.65$) the Ga diffusion coefficients show a very similar behaviour as the values for self- and As diffusion. This suggests that the vacancy mechanism dominates Ga diffusion in this region. When $x < 0.35$ gallium diffusion in $Si_{1-x}Ge_x$ is most probably dominated by the interstitial mechanism and near x = 0.5 both, vacancy and interstitial mechanisms, contribute significantly to the diffusion at 930 ^{o}C.

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Ion Tracer Diffusion and Electrical Conductivity in a PEO-NaI Polymer Electrolyte

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We studied ion transport in the polymer electrolyte $PEO_{30}NaI$ consisting of poly(ethylene oxide) (PEO) and sodium iodide in a Na-to-O ratio of 30. Depth profiles of ^{22}Na and ^{125}I were measured by means of microtome sectioning after isothermal diffusion annealing in the temperature range from 67 to 180 °C, in which $PEO_{30}NaI$ is fully amorphous. Tracer self-diffusion coefficients resulting from Gaussian or erfc fits show near-linear behaviour in an Arrhenius plot, both for Na and I. It is found that I diffuses faster than Na by a factor of 2 to 5 upon going from high to low temperatures. This is reflected by the circumstance that the apparent activation energy of I (0.29 eV) is distinctly lower than that of Na (0.39 eV). Additional information was obtained by measurements of the dc electrical conductivity using impedance spectroscopy. To this aim the frequency-dependent impedance of cylindrical $PEO_{30}NaI$ samples was recorded as a function of temperature using stainless steel electrodes. In contrast to both tracer diffusivities, the dc conductivity exhibits a pronounced Vogel-Tamann-Fulcher behaviour reflected by a downward curvature in the Arrhenius plot. As a consequence, the overall conductivity increasingly falls below the sum of the Na and I tracer diffusivity with increasing temperature. This phenomenon can be explained by the formation of neutral Na-I ion pairs which contribute to mass transport but not to charge transport. Evaluating simultaneously the different types of experimental data within a combined ion-pair/single-ion diffusion model yields besides the diffusivities of all individual species also the ion-pairing reaction constant as a function of temperature.

Application of Grow Discharge Spectrometry for Impurity Diffusion in Pure Iron

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Impurity diffusion in pure metals has been extensively studied for many elements by the radioactive tracer method and the serial sectioning techniques. However, experimental data on some elements that lack of suitable radioactive tracer for diffusion experiments are missing. Recently, the instrumental analysis for example secondary ion mass spectrometry, auge electron spectroscopy, emission spectra analysis, atomic absorption analysis and grow discharge spectrometry etc., can be applied for the microanalysis. In the present work, the grow discharge spectrometry has been attempted to determine penetration profiles for impurity diffusion of some elements in pure iron. The experimental results have been compared with those of the radioactive tracer method. The grow discharge spectrometry is found to be useful to measure the penetration profile for the impurity diffusion in metals.

Nitrogen Tracer Diffusion in Yttria Doped Zirconium Oxynitride

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Cation doped zirconium oxynitrides (for example doped with yttrium oxide, YZrON, having a fluorite-based structure) are suggested to have a fairly high nitrogen diffusivity, beside their high oxygen diffusivity. In the present work, the tracer-diffusion of nitrogen was measured in single crystalline YZrON.

Single crystalline YZrON of the nominal composition $Zr_{0.8}Y_{0.2}O_{0.97}N_{0.03}$ was obtained by annealing yttria-stabilised zirconia (YSZ) single crystals in nitrogen at 2000 K. Layers of YZrON enriched with the stable isotope ^{15}N were prepared by PLD of YSZ at 400°C and 500°C in an $^{15}N_2$ atmosphere. The nitrogen tracer-diffusion was investigated in vacuum at temperatures between 650 and 1000 K and the depth distribution of the nitrogen isotopes was analysed using SIMS. It was found that the nitrogen diffusion obeys a simple Arrhenius law, with an activation energy around 2 eV. The results were compared to previous results where the tracer ^{15}N was implanted in YZrON with varying nitrogen content (1.32 to 1.55 wt%).

From the pre-exponential factor it is suggested that nitrogen diffusion occurs via anion vacancies.

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Diffusion of Li and B in Refractory Materials Studied with the Neutron Depth Profiling Technique

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Lithium has three short-lived isotopes ^{8,9,11}Li (840, 178 and 9 ms half-life) of high interest for nuclear physics. The presently best Li beams produced at the isotope separation on-line facility ISOLDE are extracted from 2 µm thick Ta foils kept above 2400 K. Still, a big fraction of the produced isotopes decay before being released from the foils. On the other hand the thermal cycling due to the pulsed proton beam impact (several GW/cm^2 beam power within 2 µs) provokes that the foils sinter together within few days, slowing down the release even further. We are therefore investigating alternative target materials. The sintering might be reduced using elements with higher melting point (W, Re) or by coating the surface of metal foils with a refractory compound (e.g. by carbidization to HfC, TaC, WC or oxidation to HfO_2). To find out how this affects the Li release we started recently a program to measure Li diffusion in these materials by thermal neutron depth profiling of ion implanted ^{6}Li before and after isochronal annealing. Radioactive ion beams of ^{8}B ($T_{1/2}$=770 ms) would have interesting applications, but presently no ISOL beams of boron exist. Elemental boron has strong bonds with most elements used in high-temperature target and ion source units (C, N, O, metals). Hence, a rapid desorption can only be guaranteed by using a chemical evaporation technique, e.g. by supplying sufficient amounts of fluorine to form the volatile molecules BF_x. The required vapor pressure of fluorine could be created in-situ by heating a fluoride, which could serve simultaneously as spallation target for the ^{8}B production. Therefore we studied with neutron depth profiling and isochronal annealing the release of ion-implanted ^{10}B from CaF_2, the highest-melting fluoride.

The Role of Intrinsic Defects for the Diffusion of Ag and Cu in CdTe

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A model describing the unusual diffusion profiles observed for Ag and Cu in CdTe [1] is presented. For the diffusion experiments, the radiotracers ^{111}Ag and ^{67}Cu were implanted into one side of a CdTe crystal either at the mass separator of the university of Bonn (80 keV) or at the isotope separator ISOLDE at CERN (60 keV). For Ag and Cu the measured diffusion profiles critically depend on the respective external conditions during diffusion and during sample pre-treatments performed in some cases.

Thus, the Ag profile in a 0.8 mm thick crystal obtained after diffusion at 800 K under Cd pressure is symmetrically with respect to the center of the crystal followed by strongly Ag depleted layers of about 250 μm width towards both surfaces; it should be recalled that the implanted diffusion source was located on one side of the crystal at a depth of about 30 nm. In contrast, the Ag concentration is enhanced near the surface and depleted in the interior of the crystal, if the Ag diffusion is performed under Te vapour. In particular, in the first case these effects are strongly pronounced in crystals pre-annealed under Te vapour and in untreated crystals and they can be completely switched off by pre-annealing under Cd vapour.

The various Ag and Cu diffusion profiles observed under different external conditions can be explained to a large extent in the framework of a model using the interaction with the intrinsic defects V_{Cd} and Cd_i. As will be shown, the Ag (Cu) profile essentially reflects the profile of the Cd vacancies. The model will be discussed in terms of the deviation of the CdTe crystal from stoichiometry and the change of the stoichiometry during thermal treatment under the variation of the external conditions.

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Analysis of the Time Dependence of Demixing of Oxides (A,B)O in an Oxygen Potential Gradient and an Electric Field

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Most treatments of demixing in oxides focus only on the steady state condition reached only after long times. In this paper, we address the time dependence of the demixing of the cations in mixed oxides of the (A,B)O type where demixing can occur in either an oxygen potential gradient or an electric field (high current conditions). Assuming an initially random distribution of cations, we make use of the sum-rule relation between phenomenological coefficients to derive expressions (which are then solved numerically) for the time dependence of the demixing profiles. We also use Monte Carlo computer simulation to verify these demixed concentration profiles. Two extreme cases, one where the system is 'open' and the cation vacancies are in contact with the surface, the other where the system is 'closed' and the cation vacancies respond only to local forces, are both addressed. It is shown that the concentration profiles evolve quite differently for these two cases. Appropriate predictions are made for real oxide systems that might differentiate between the two cases.

Influence of the Lacunar Diffusion on the Initial Stages of Precipitation of Supersaturated Cu-2%Be-0.3%Cd Solid Solution

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The effect of small addition of Cd atoms on the Vickers isothermal microhardness curves has been studied for the supersaturated solid solution Cu-Be2%-Cd-0.3%(weight.) In the initial stage of precipitation GP zones are formed. Its volumic fraction is determined for different thermal ageing times (0.33 ks to 10 ks) ang kinectic of GP formation is given.

The results obtained shows that Cd atoms has an accelerating effect on the GP formation during thermal treatment with a pic of GP formation at 473K. This is due to the supersaturation free vacancies present at ambient temperature in Cu matrix and the strong binding energy between added Cd atoms and vacancies. Our results are in good agreement with Kimura and Hasiguti formula based on solid state atoms diffusion mechanisms .

A Monte Carlo Study of Precipitation Kinetics in Al-Zr-Sc Alloys

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Zr and Sc precipitate in aluminum alloys to form the Al_3Zr, Al_3Sc, and $Al_3Zr_xSc_{1-x}$ compounds, which at low super-saturations of the solid solution have the $L1_2$ structure. The aim of the present study is to model at an atomic scale this kinetics of precipitation and to build a mesoscopic model based on classical nucleation theory so as to extend the field of super-saturations and annealing times that can be simulated.

In this purpose, we use some ab-initio calculations and experimental data to fit an Ising model describing thermodynamics of the Al-Zr-Sc system. Kinetic behavior of this system is described by means of an atom-vacancy exchange mechanism. This allow us to simulate the kinetics of precipitation in Al-Zn-Sc alloys with a kinetic Monte Carlo algorithm.

In binary Al-Zr and Al-Sc systems, these kinetics are used to test the classical nucleation theory. In this purpose, we deduce isotropic interface free energies and nucleation free energies from our atomic model. Different mean-field approximations as well as low temperature expansions are used to obtain these parameters. The classical nucleation theory is coherent with the kinetic Monte Carlo simulations when Cluster Variation Method or low temperature expansions are used: it manages to reproduce the cluster size distribution in the metastable solid solution and its time evolution as well as the steady-state nucleation rate.

In ternary Al-Zr-Sc system, kinetic Monte Carlo simulations allows us to show that Zr mainly affects nucleation whereas Sc influences nucleation as well as growth and coarsening stage. The main consequence is that a Zr addition to an Al-Sc alloy leads to finer precipitates and increases their density, in agreement with available experimental kinetics of precipitation.

Effects of High Hydrogen Pressure and Fugacity on a $Pd_{90}Pt_{10}$ alloy

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The Pd-alloys system has attracted great interest because of their potential range of technological applications and also by their excellent physical properties in the presence of hydrogen. The aim of this work is to study the phase transformation induced by hydrogen in a $Pd_{90}Pt_{10}$ alloy submitted to a high hydrogen pressure and high fugacity.

A button of $Pd_{90}Pt_{10}$ alloy was prepared in an arc furnace with an inert atmosphere. The sample was repeatedly re-melted to homogenize the composition. Subsequently, the button was cold worked and then heat treated at 800 °C for 1h. The resulting sheet-shape samples were submitted to electrochemical hydrogen permeation testing using NaOH, 0.1 N as electrolyte. Cathodic charging currents ranging from 0.1 to 50 mA were applied during the hydrogen permeation tests. Another group of samples was submitted to an elevated hydrogen pressure of 5GPa at 800°C for 5h. The phase transformation analyses were performed by X-ray diffraction, XRD.

It was observed that both the hydrogen diffusivity coefficient and solubility were dependent on the cathodic current applied. For applied currents up to 10 mA a slight deviation in the hydrogen permeation curve was observed which suggested hydride formation during the hydrogen permeation test. The XRD results showed two sets of peaks after hydrogenation. The new set of peaks corresponded to phase separation, which took place when the samples were submitted to high cathodic currents. The same type of behavior was observed for the samples submitted to high hydrogen pressure and when the phase separation was due to the superabundant vacancies formed by the hydrogenation, which reduced the activation energy for diffusion of Pt in the Pd matrix.

Formation of Intermetallic Layers at the Interface of Iron-chromium Alloys and Molten Aluminium

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Two intermetallic-compound layers are formed at the interface between a Fe-Cr alloy (10 or 25 mass % Cr) and aluminium saturated with the alloy components. A compact uniform layer adherent to the solid alloy base consists of the Fe_2Al_5 phase. A porous non-uniform layer bordering with aluminium is mainly the Fe_2Al_7 phase. The latter actually consists of separate grains weakly linked with each other. Hence, its formation might be partly a result of a solid-state chemical reaction and partly a consequence of crystallization from the melt. On the contrary, the layer adjacent to the alloy base is formed entirely in the course of another solid-state chemical reaction. Under conditions of simultaneous dissolution in pure liquid aluminium only the compact Fe_2Al_5 layer occurs, while other intermetallic phases (Fe_2Al_7, $FeAl_3$, $FeAl_6$, etc.) exist as inclusions in the aluminium matrix. Dissolution causes a three-fold decrease in the Fe_2Al_5 layer thickness compared to the case where a Fe-Cr alloy is in contact with a saturated melt and hence no dissolution takes place. In the case under consideration, a general mathematical equation describing the layer-growth kinetics under conditions of its simultaneous dissolution in the liquid phase (V.I.Dybkov, 'Reaction diffusion and solid state chemical kinetics', The IPMS Publications, Kyiv, 2002) assumes a simple form suitable for estimating the layer thickness, namely: $x_t = k_1/b_t$ where k_1 is the layer growth-rate constant and x_t is the maximum thickness that can be reached by the growing intermetallic layer in time t if the rate of its dissolution in the time range $0 - t$ remains constant and equal to b_t. Experimental values of the Fe_2Al_5 layer thickness are in fairly good agreement with those estimated according to this equation.

Diffusion Coefficients of Iron and Chromium from Fe-Cr Alloys into Molten Aluminium

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The dissolution process of any solid alloy in a liquid-metal bath is characterized by the saturation concentrations or solubilities, c_s, of the alloy components in the liquid phase and their dissolution-rate constants, k. In the case of a binary alloy, the dissolution rate constants can be either identical for both components (non-selective dissolution) or different (selective dissolution). Dissolution of iron-chromium alloys (10 and 25 mass% Cr) in an aluminium melt was found by the rotating-disc technique to be non-selective. At 700°C, the saturation concentrations were determined to be 2.5 ± 0.2 mass% Fe and 0.28 ± 0.03 mass% Cr for an Fe–10 mass% Cr alloy and 2.2 ± 0.2 mass% Fe and 0.72 ± 0.06 mass% Cr for an Fe–25 mass% Cr alloy. Note that the solubility limits of iron and chromium in liquid aluminium in the Al–Fe and Al–Cr binary systems at this temperature are 2.5 mass% and 0.72 mass%, respectively. The former value coincides with the saturation concentration of iron for an Fe–10 mass% Cr alloy, while the latter corresponds to the saturation concentration of chromium for an Fe–25 mass% Cr alloy. At an angular disc rotation speed of 24.0 rad s^{-1}, the values of the dissolution-rate constant are $(4.2 \pm 0.2) \times 10^{-5}$ m s^{-1} for an Fe–10 mass % Cr alloy and $(3.0 \pm 0.2) \times 10^{-5}$ m s^{-1} for an Fe–25 mass% Cr alloy. Corresponding diffusion coefficients were estimated from these values of k to be 1.4×10^{-9} m^2 s^{-1} for the former alloy and 0.9×10^{-9} m^2 s^{-1} for the latter. The diffusivities thus obtained characterize the rate of cooperative diffusion of iron and chromium atoms from the Fe–Cr alloys across the diffusion boundary layer at the solid-liquid interface into the bulk of the aluminium melt. As dissolution is non-selective, these are identical for both elements.

Transient Liquid Phase Diffusion Bonding of Nickel Base Superalloy Rene 80

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Transient liquid phase diffusion bonding has been used to join a nickel base superalloy (Rene 80) using an amorphous metal interlayer with chemical composition of Ni- Cr- B -Si . The Rene 80 alloy specimens were joined at 100 ±5 ^{0} C for various hold times, both under vacuum and commercial argon atmosphere. After completion of bonding process the specimens were cooled to room temperature and then homogenized at 1206^0 C for 1and 2 hours. Metallographic examination of bonds made in commercial argon atmosphere shows pores and cavities at the bond / parent metal interface and these pores increase with increasing bonding times. This was related to the reaction of parent alloy with oxygen impurities before melting of the interlayer. However, bonds made in a vacuum atmosphere show the formation of a continuous microstructure with that of the parent alloy. EDAX analysis of bonds made in various condition shows that bonds made in vacuum and then homogenized for 2 hours at 1206^0 C , have the same alloying elements distribution as that of the parent alloy.

Thermal Stability of NiAl-base Coatings for High Temperature Applications

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Aluminide diffusion coatings act as a remedy against the aggressive environments in which modern aero-gas turbines operate. Platinum addition to basic aluminide coatings significantly improves the oxidation resistance of these coatings. The increase in operating temperatures of industrial energy systems and gas turbines, has led to the extensive use of coatings capable of providing improved service life. Interdiffusion plays a critical role in understanding the integrity of such coatings.

The mathematical model for interdiffusion in multi-component open system which allows for the description of a wide range of processes (including processes stimulated by reactions at interfaces) is employed for the modeling of interdiffusion in the Pt-modified β-NiAl coatings. Using the inverse method the intrinsic diffusivities of Ni, Al and Pt were calculated. These diffusivities were subsequently used for modeling of thermal stability of Pt-modified aluminide coatings in air and in argon atmosphere.

Multi-scale Modeling of Isochronal Resistivity Recovery Experiments of Electron-Irradiated α-Fe

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Isochronal resistivity recovery experiments, performed on pure Fe samples irradiated by electrons provide quantitative but indirect information concerning the migration, annihilation, aggregation and dissociation of point defects [1]. Their interpretation is therefore a subject of controversy. In spite of previous theoretical efforts devoted to understand these events, some questions are still open, such as the nature of stage II - experimentally assigned to migration of small self-interstitial clusters - and of the extra stage at 500-600K which appears only after high dose irradiation.

We propose here a multi-scale modeling approach to simulate this type of experiment. The SIESTA method is used to perform a systematic ab initio study of the stability and mobility of various defects in Fe: self-interstitial atoms (SIAs), vacancies, and small SIA- and vacancy-clusters. These results are then used as input data for an Event based kinetic Monte Carlo model (JERK) to simulate the defect population evolution - and the corresponding variation of sample resistivity - over large time and length scales, following closely the experimental conditions.

We obtain an excellent agreement between simulations and experiments. Recovery stages are well reproduced and we clearly attribute the stages I_E, II, III and that at 500-600K to SIA, di-SIA (tri-SIA), vacancy (and small vacancy cluster) migration, and vacancy cluster dissociation respectively. The irradiation dose effects are also properly reproduced.The present study allows clarifying some discrepancies between experiments and previous theoretical results while the mobility of larger SIA and vacancy clusters are also disscused in light of the comparison between experiment and theory.

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Phase formation under pulse loading

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Pulse loading of diffusion couples, consisting of metals with full mutual solubility, leads to so-called anomalous mass-transfer – formation of huge “diffusion zone” (tens or even hundreds microns after 1-1000 microseconds). Possible mechanisms of this phenomenon are still under discussion.

Even more interesting is behavior (under pulse loading) of couples with limited equilibrium solubility and with intermetallic phases at equilibrium phase diagram. Among other couples, nonequilibrium phase diagrams were determined for following interactions:
Cu- Ni, Al, Mo, Fe, Ti, Zn, Sn, Cd, Ga; Fe-Cr, Mo, Nb, V, Ti, Al, Sn; Ni-Zr, Co-Ti, Ti-Mo.

General regularity is that pulse loading under low temperatures usually leads to formation of the broad metastable solid solutions without traces of intermetallics. Under higher temperatures, combined with high deformation rates, intermetallics also can form.

We present simple analytical model for intermetallic formation under pulse loading.

We also present results of MD-simulation of pulse loading by shock wave, leading to formation of nanostructure, making possible intermixing at nano-level.

Atomistic Monte Carlo Simulations of Homogeneous and Heterogeneous Precipitation of NbC in Steels

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The precipitation of niobium carbides in industrial steels is commonly used to control the recrystallization process or the amount of interstitial atoms in solid solution. It is then important to understand the precipitation kinetics and especially the competition between homogeneous and heterogeneous precipitation, since both of them have been observed experimentally, depending on the alloy composition, microstructure and thermal treatments. We propose Monte Carlo simulations of NbC precipitation in α-iron, based on a simple atomic description of the main parameters which control the kinetic pathway :

- realistic diffusion properties, with a rapid diffusion of C atoms by interstitial jumps and a slower diffusion of Fe and Nb atoms by vacancy jumps;
- a simple model of grain boundaries and dislocations which reproduces the equilibrium segregation properties of Nb and C;
- a point defect source which drives the vacancy concentration towards its equilibrium value.

Depending on the precipitation conditions, MC simulations predict different kinetic behaviours, including homogeneous and heterogeneous NbC precipitation, early segregation of C atoms and its importance as a first stage for NbC precipitation, wetting phenomena on grain boundaries, transient precipitation of metastable carbides, etc.

Phase Transformations Study of $Se_{98}In_{1.5}Sn_{0.5}$ Chalcogenide Glass Before and After Slow Neutron and High Energy C^{12} Ion Irradiation.

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Results of phase transformations of $Se_{98}In_{1.5}Sn_{0.5}$ chalcogenide glass under non-isothermal condition, before and after slow neutron and high energy C^{12} ion irradiation, using differential scanning calorimeter (DSC) have been reported and discussed. Upon slow neutron irradiation, for different exposure time, the crystallization activation energy E_c and the glass transition temperature T_g are found to increase. This has been attributed to the structural change upon doping by some Sn atoms through nuclear transmutation process. The effects of high energy C^{12} ion irradiation on the structure of $Se_{98}In_{1.5}Sn_{0.5}$ glass have also been monitored by the evaluation of the crystallization parameters, T_g and the onset temperature of crystallization $T_{c.}$ Both T_g and T_c are found to decrease due to the introduction of defects upon high energy C^{12} ion irradiation.

Calculation of Surface Self-diffusion Coefficients from AES Data on Decay of Thin Metal Films

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Thin films have a very high surface to volume ratio, which produces a large driving force reducing the surface area. Due to diffusion mass transfer, the thin film changes its shape and becomes discontinuous. The decomposition of a thin continuous film into a collection of beads occurs in three steps: the fluctuation of the film thickness with the formation of voids, the void growth (until they overlap) which leads to formation of island film, and transformation of island shape to equilibrium one. In this paper we propose a simple method for calculation of surface self-diffusion coefficients using kinetic data on the second and third stages of film decay.

In calculations we took into account equilibrium wetting angle of the film on a substrate. For the kinetics of void growth and for decrease of island area due to shape transformation we have obtained, respectively:

$$\rho^{\alpha}(\tau) = \rho_0{}^{\alpha} + \kappa\tau \qquad \text{and} \qquad \sigma(\tau) = \sigma_0 - K\tau^{\beta}$$

where $\rho(\tau)$ is dimensionless void radius, $\rho = r / h$, $r(t)$ is the current void radius, h is the film thickness, τ is the dimensionless time, $\tau = Bt/h^4$, $B = D_s\gamma\Omega^2 n_0/k_BT$, t is the current time, γ is the surface tension, Ω is the atomic volume, n_0 is the surface atomic density, $\sigma(\tau)$ and is a dimensionless island area, $\sigma = S / h^2$, S is the island area, κ, K, α, and β are numerical coefficients tabulated for various wetting angles.

The kinetic data on decay of Au and Pd thin films on sapphire substrates were obtained using AES. By *in situ* monitoring intensity of the AES signal from the film we could easily distinct the second and the third stages of the decay. The surface self-diffusion coefficients and the activation energies are calculated and discussed compared to those obtained by other methods.

Peculiarities of Diffusion Mass Transfer in System Fe[Cr]-Pb[O]

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Processes of high-temperature interaction of Cr-containing steel with lead melt containing oxygen are theoretically and experimentally investigated. The structure and composition of oxide layer formed on the surface of steel EP-823 exposed to stagnant lead melt containing oxygen ($C_{O[Pb]} \approx 10^{-5}$- 10^{-6} mass.%) at 650°C, for 3500 h are investigated. It is determined that thin (≤ 1000 Å) oxide layer enriched in chromium is formed on the steel surface under the test conditions described herein. Oxide layer is intensively formed on the grain boundaries and distributes on whole surface in time. The formed oxide is protective against melt penetration into steel matrix. Iron migrates through the chromium oxide layer after long-term exposure and is not only being dissolved in the melt but also forms the oxides in the reaction zone. The kinetics of diffusion dissolution of iron in lead melt with the iron-oxygen chemical interaction taken into account is analytically investigated. Assumed that oxygen serves as a "trap" for iron ions and pulls them out from the diffusion flux Fe–O complexes are considered as separate slow-moving components of the melt. We consider diffusion equations with an additional term that describes the volume reaction between Fe and O in melt and boundary conditions accounting for the time dependence of oxygen concentration at the interface of both melt and metal sides. Task resolution is obtained in analytical form in terms of Laplace transformation. The analysis of the obtained relations gives the basis to assert that in case of dissolution of iron in the lead melt containing "oxygen traps" the diffusion zone is less than that in the conditions of pure dissolution (without "traps"). However the whole concentration of iron both on the surface of the oxide layer and in the contact zone of melt is increased.

Decomposition of Solid Solution and Formation of Nanostructure During High-PressureTorsion of Al–Zn, Al–Mg and Al–Zn–Mg Alloys

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Structure and phase composition of binary Al–Zn, Al–Mg and ternary Al–Zn–Mg alloys were studied before and after high pressure torsion (HPT) with shear strain 300. The size of (Al) grains and crystals of reinforcing second phases decreases drastically after HPT reaching nanometer range. As a result of HPT, the Zn-reach (Al) supersaturated solid solution decomposes completely and reaches the equilibrium state corresponding to room temperature. The decomposition is less pronounced for Al–Mg and Al–Zn–Mg alloys. We conclude that the severe plastic deformation of supersaturated solid solutions can be considered as a balance between deformation-induced disordering and deformation-accelerated diffusion towards the equilibrium state.

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The Role of Diffusion in Superplasticity and Brittleness of Fine-grained Binary Eutectics

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Mechanical behaviour of phase boundaries (PB), stability of defects and microstructure in heavily deformed binary eutectics at room temperature (Al-Sn, Zn-Sn, Pb-Sn, Cd-Sn, Bi-Sn) have been investigated. The room temperature for all eutectics was ~ 0.5 T_s, which was enough for the development of the surface and grain boundary diffusion. Experiments were carried out on the atomically clean surfaces of alloys and on the bimetallic joints with clean interface. It has been shown that after heavy deformation in all eutectics the phases are strengthened and relaxation processes occur mainly on the boundaries. For superplastic eutectics with low phase boundary energy the intensive development of the diffusion – controlled processes of self healing, sintering, overlaying, dissolution-precipitation and correlated accommodation on the PB was observed. Estimates for Pb-Sn and Bi-Sn eutectics show very high values of diffusion coefficient along PB that are typical for liquid. These diffusion processes, directed to restoration of a contact, are the reason of softening of phase boundaries and superplastic viscous flow.

It has been shown, that for the eutectics with high PB energy (Al–Sn, Zn–Sn) the interphase boundary sliding occurs by means of the dislocation gliding, followed by a remarkable strengthening and accompanied by the formation of narrow PB cracks with sharp angles. In these eutectics despite of enough high temperature diffusion healing of micropores and cracks on phase boundaries does not develop also deformation defects are stable. Such deformed structure of PB defines low temperature brittleness and hydrogen diffusion in eutectics with high PB energy. Distinctions in deformation behaviour of investigated eutectics are considered from positions of thermodynamics of the adhesion phenomena.

Ageing Kinetics of Beryllium Bronze in the Constant Magnetic Field

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Beryllium bronze BrB-2 samples, after water hardening at 800°C, have been annealed with the purpose of ageing in vacuum ~ 10^{-3} Pa at different temperatures (from 250 up to 500 °C) during 15-120 min in constant magnetic field (CMF) of 558,6 kA/m and without it.

X-ray diffraction phase and structure analysis of samples from BrB-2 past thermal and magnetic annealing is performed. On the basis of X-ray diffraction phase analysis data the parent matrix lattice parameter and the concentration of the residual matrix are designed as a function of time, annealing temperature and CMF intensity.

On the basis of the analysis of (111) and (222) diffraction line plrofiles the sizes of coherently dissipating blocks, density of dislocations and sizes of relative average microdeformation of a lattice are calculated. Their temperature, time and field dependences are established.

The analysis of the given data shows that imposing of CMF on the process of ageing of beryllium bronze BrB-2 results in the formation of more uniform and fine disperse structures.

The conclusion is made, that imposing of CMF increases the completeness of a leave of beryllium from a parent solution in enrichment zones and improves physical and mechanical properties of a material due to changes of thin structure parameters of material.

An Opportunity of Introduction of Critical Indices in the Description of Nickel- 63 Diffusion in Monocrystal Siliceous Iron in a Constant Magnetic Field

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The critical phenomena near the second-order phase transitions in solids represent the most interesting field for researches including diffusion studies. In the present work there has been made an attempt to introduce critical indices for the description of diffusion of ^{63}Ni in Fe-Si single crystal for two crystallographic orientations in constant magnetic field (CMF).

Working [100] and [110] surfaces of the cube samples with an edge 10 mm long were mechanically grounded and polished. The samples were subsequently annealed for an hour in vacuum ~ 10^{-4} Tor in order to remove mechanical pressure and to stabilize the structure. The films of ^{63}Ni ~ 0,05 μm thick were electrolitically deposited on the surfaces prepared in the described way. Diffusion anneallings were carried out in the phase transition domain in vacuum ~ 10^{-5} Tor with temperature interval of 740-800 ^{o}C and CMF of 0-7 kOe. Diffusion coefficients were measured by means of P.L. Grusin's method.

It is shown, that critical indices for a magnetic part of the activation free energy for diffusion in absence of CMF practically do not depend on the orientation of the samples and equal 1,1-1,2.

Upon imposing CMF the critical indices behave unstably and the definite description of diffusion process is not always possible.

Determination of Diffusion Coefficient in Al-Li Alloy

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The strengthening of binary Al-Li alloys, with an atomic concentration in the range 6%-14%, is caused by the precipitation of a metastable coherent ordered δ'Al_3 Li phase.

The formation kinetics of the δ' phase is established using a method based on microhardness measurements.

During the coarsening, the perfect coherency between the δ' phase and the α solid solution matrix and the small surface free energy of the δ' / α interface ensures that precipitates retain their spherical shape. Then, during later aging stages when the phase transformation still being far from complete, the supersaturation obeys the relationship given by the LSW theory of particule coarsening:

$$x_m - x_e = (kt)^{(-1/3)} \text{ where } k = D(RT)^2 / 9\sigma^2 x_e^{\,2} V_m$$

x_m is the mean concentration of solute in the matrix, x_e the equilibrium solute concentration, V_m molar volume of precipitate, σ the free energy of the particule – matrix interface and D, the diffusion coefficient of the solute in the matrix is detemined for 150°C aging temperature.

Liquid Gallium Penetration along Grain Boundaries in pure Al and Al-Ga Alloys

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The kinetics of liquid Ga penetration along grain boundaries in pure Al and Al-Ga alloys with concentration (0.7, 1 and 3% mass. Ga) was studied. The study was performed in two regimes: in situ observation under light microscope at temperature 42°C and observation of quenched state after exposition at the same temperature.

It was shown that crack-like channels filled by liquid Ga formed along all grain boundaries. Their width was about 1-3 μm. In situ observation under light microscope showed that the channels propagated with the rate about 10 $\mu m \cdot s^{-1}$ just ahead of liquid Ga front spread over the surface.

Investigation of quenched state showed that in all samples channels grew following linear kinetics and the propagation rate depended on Ga concentration in alloys: 14.2 μm/s for pure Al, 8.0 μm/s for Al with 0.7 % Ga, 9.3 μm/s for Al with 1 % Ga and 9.8 μm / s for Al with 3 % Ga.

Non-monotonous behavior of propagation rate in dependence on Ga concentration in alloys is explained in terms of a competition between driving force of crack propagation and stress to rapture, both depending on Ga concentration.

The Model of Liquid Channel Growth with Excessive Chemical Potential as a Driving Force

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This paper is dedicated to description of liquid channel growth process when a solid polycrystalline metal is in contact with liquid one. To describe the properties of atoms on grain boundary and on the surface excessive chemical potential ($\Delta\mu$) as compared with bulk one is used. It includes excessive energy of grain boundary, coherent strain energy, but does not include curvature of the surface.

Taking into account that in this case the kinetics of atoms dissolution depends on excessive chemical potential and surface curvature the equations similar to Mullins equation were obtained

$$\frac{\partial y}{\partial t} = -DC_0 \frac{a}{b}\left(\sqrt{1+y'^2}\,\frac{\Delta\mu(x)}{RT} - \frac{y''}{\left(1+y'^2\right)}\frac{\gamma\Omega}{RT} \right)$$

Here y (x) is depth of the channel on distance x from grain boundary; t is time; D and C_0 are diffusion coefficient and concentration of saturation in liquid; a is interatomic distance; b is distance from surface in liquid when concentration is equal to C_0; γ is a solid-liquid surface tension, Ω is an molar volume of solid, $\Delta\mu(x)$ is a function, which describes excessive chemical potential along solid-liquid interface.

Depending on type of F function the different morphology and growth kinetics of channels can be obtained.

In the case when $\Delta\mu$ acts at GB only, two limit cases were analysed. Mullins solution was obtained for $y' \ll 1$. In the second one ($y' \gg 1$) thin (2-3 interatomic distance) channels can grow with constant rate.

Role of Cu at the Ni-Ag Interface on the Reactive Solid State Dewetting by Cavitation in the System Ag-Ni-O

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Recent results are presented showing that the presence of a thin copper layer deposited under ultra-high vacuum at a nickel-silver interface can suppress the process of reactive solid state dewetting by cavity formation, which was previously reported.
Indeed when thick silver films deposited onto Ni substrates are annealed at high temperatures in an oxygen atmosphere dewetting occurs because a NiO layer is formed at the Ag-Ni interface as a consequence of oxygen diffusion through the silver film. Cavity formation at the Ag-NiO interface had been shown to be the main mechanism of dewetting for short annealing times [1,2].
A study of the role of this interface layer in the control of the kinetics processes associated with NiO growth and cavity formation will be presented.

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The Peculiarities of the Radiation – Enhanced Diffusion Processes in Metals with Consideration of the Impurities and Grain Boundaries Effects

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In the framework of previously developed views on radiation – enhanced diffusion (RED) kinetics [1, 2] the effects of impurities and grain boundaries on RED are considered. The approximate solution of kinetic equations for RED and radiation – enhanced grain boundary diffusion (REGBD) with the consideration of the formation and decomposition reactions of vacancy – impurity atom complexes for “accelerating” and “retarding” impurities are derived. The approximate model of REGBD predictions in metals is presented. The estimations of RED and REGBD coefficient changes for different impurity content in some transition metals are obtained. The estimations of the effective RED coefficients in terms of the volume and grain boundary contributions for some transition metals and actinides with impurities are derived. The mechanisms of RED and REGBD in metals are discussed.

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Temperature Dependent Cluster Model of the Cole-Davidson Relaxation Response

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Some new theoretical results regarding the dielectric relaxation and the glass transition are given. Based on the probabilistic cluster model of the relaxation phenomenon, we propose a possible way to pass from the Debye to the Cole-Davidson response. We show that the probabilistic characteristics of the relaxation contributions to both responses, given by individual clusters, can be substituted by deterministic quantities describing the average relaxation rate B(T) and the average cluster size N(T). The explicit functions on temperature T result from the behaviour of the of the loss peak frequency $\omega_p(T)$ for the relaxing system. We present the results for both "strong" and "fragile" glassy systems.

Effect of Grain Size and Grain Boundary Character Distribution (GBCD) on Hydrogen Permeation in Nickel Membranes

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Hydrogen transport through nanocrystalline and polycrystalline nickel membranes has been investigated by electrochemical hydrogen permeation. Nickel samples with different grain size were obtained by annealing nanocrystalline nickel membranes between 200^0C and 900^0C. After annealing, the grain size of nickel membranes increases and yields a gradual texture change in the nickel membrane from (100) fiber texture to (111) recrystallization texture. When the charging current was increased, the permeation current for the nano-Ni membranes increased more rapidly, and then reached a high steady state level. The hydrogen diffusion coefficients of the nano-nickel membranes are dependent on hydrogen concentrations (charging current). The diffusivity of hydrogen is six times higher in polycrystalline membranes than in single crystal membranes, and increases again 6 times in nanocrystalline membranes. As the grain boundaries volume become a small portion of the sample volume after annealing at 800 ^{0}C and 900 ^{0}C, large changes in the grain size cannot even be noticed by measuring the rate of diffusion of hydrogen.

Ageing Kinetics of Al.-4.7 % Cu Alloy. Dilatometric and DTA Studies

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Studies of transformation kinetics during ageing of Al-4.7 % Cu were performed by means of dilatometric and DTA methods. Dilatometric method was used for studies of isothermal ageing , DTA for studies of ageing during isochronal heating. In order to determine isothermal transformations kinetics JMA (Johnson – Mehl – Avrami) equation was applied, for isochronal heating transformation kinetics Kissinger method was used. Ageing of Al- Cu alloys consist of precipitation processes and dissolution processes that overlap each other. These processes during isothermal ageing were distinguished with help of the time exponent n of JMA equation that is very sensitive for transformation mechanism change. During isochronal ageing precipitation processes produce heat, dissolution processes consume heat. That helps to distinguish each other. Results obtained during isothermal studies were in agreement with isochronal heating studies. Activation energies for precipitation processes at 440-530 K temperature range were order of 110 kJ/mole and agreed with values obtained before. For precipitation processes in 650- 700 K temperature range these energies were order of 275 kJ/mole. Results were discussed in view of the literature data.

The Evaluation of the Recrystallized Grains in the Friction Stir Welded 6061 Al Alloys

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Friction Stir Welding(FSW) is the one of the solid state bonding technique, which means the joining process is completed below the melting temperature of welded materials. The diving force of FSW is the severe plastic deformation and accompanying frictional heat caused by the contacting rotating welding tool with welded specimens.

The dynamic recrystallization occurred in the weld zone and this region shows the very fine and equaxed grain structure.

Many articles have suggested that the equaxed grains at the weld center are nucleated by dynamic recrystallization during the stir of the material. After the nucleation, there is possibility that the dynamically recrystallized grains experience static grain growth during the cooling of the thermal cycle. If the dynamically recrystallized grain grew statically, the equation for the static grain growth should be satisfied in the friction stir welds

In this study, the residual microstructure of the weld zone (stir zone) was systemically evaluated with various welding parameter (welding speed, tool rotation speed and post weld aging heat treatment) and the measured the recrystallized grain size according to the static grain growth and also effect on the mechanical properties of weld zone.

Bonding interface in friction welded Al alloys and carbon steel after annealing heat treatment

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Friction welding method has many advantages compared to the fusion weld method and specially reaches high joint strength about the dissimilar materials joint. These results are mainly acquired because this welding technique are solid-state bonding technique and have a repulsive stage (upset stage).

The interfaces of Al alloy and steel can form many of intermetallic compounds, which badly effect on the joint strength. So in this study, we evaluated the interface phenomena and growth kinetic of intermetallic compound with various friction welding condition and post welding annealing treatment.

Diffusion in Multicomponent and Multiphase System: Modeling of Zinc Hot-Dip Galvanizing Process

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An understanding of interdiffusion in multicomponent and multiphase system is essential for prediction of phase growths during zinc hot-dip galvanizing process. In this paper, by using the Nernst-Planck flux formula and the Darken drift flow concept an interdiffusion model has been postulated. Transfer factors for diffusion through interfaces have been introduced in order to quantitatively describe diffusion in multiphase system. On the ground of the thermodynamic data implemented into the model the kinetic simulation of phase growths has been obtained in the system Fe-Zn. The simulation results agree well with experimental observations.

p^+-CdB_2 - n-CdF_2 and p^+-Si – p-CdB_2 - n-CdF_2 Diffusion Heterostructures

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Ionic semiconductor CdF_2 is of extraordinary interest for the modern optics and optoelectronics because of a record band-gap, 7.8 eV, from all wide-gap semiconductors. The goal of this study is to apply the short-time diffusion of boron into CdF_2 to prepare the quantum-size p^+-CdB_2 - n-CdF_2 and p^+-Si – p-CdB_2 - n-CdF_2 heterostructures.

The p^+-CdB_2 - n-CdF_2 heterostructures have been prepared by short-time diffusion of boron from gas phase at the temperature of 620°C, whereas p^+-Si – p-CdB_2 - n-CdF_2 heterostructures were grown by the CVD method using the evaporation of the silicon heavily doped with boron that duffuses into the CdF_2 bulk during the process of growth of the silicon alloy. After short-time diffusion of boron the CdF_2 bulk was transformed into the n-type by the thermal coloring method. Strong thermal coloring has been shown to give rise to the lowest leakage currents in the heterostructures prepared in comparison with the application of the weak thermal coloring process.

Using the quantum conductance technique, it was shown, that the p^+-CdB_2 and the p^+-Si alloys contain the self-assembled nanostructures of the p-type. The forward branches of the CV characteristics of heterostructures exhibit the CdF_2 band-gap, 7.8 eV, as well as reveal the negative resistance part under the forward voltage value above 4 eV that corresponds to the electron affinity for both the silicon and CdF_2 crystals. Besides, the forward branches of the CV characteristics have been made it possible the identification of the CdF_2 valence band in details, which is revealed by single-hole tunneling from silicon self-assembled quantum wells. The electroluminescence in the visible range of optical spectrum that results from the irradiative recombination of electrons tunnelling from n-CdF_2 with holes localised at the subbands in the quantum well forming by the p^+-CdB_2 - n-CdF_2 interface has been found under the forward bias.

Diffusion as Stability-limiting Factor in FINEMET Type Materials

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The diffusion-controlled grain growth plays a fundamental role in a structural stability of nano-crystalline alloys. To understand the structure stability of nano-materials, it is essential to find the process with the slowest kinetics.
The new diffusion characteristics related to $Fe_{73.5}Si_{13.5}Nb_3B_9Cu_1$ FINEMET alloy are reported in this paper. They offer – together with literature data – a more complete picture revealing the process with the slowest rate.
The diffusion of ^{67}Ge, representing well the Si behavior in FINEMETs, was measured in the model Fe-Nb binary system which was chosen to simulate diffusion barrier in the given nano-crystalline/amorphous composite material.
As model materials, the pure iron, eutectic Fe_2Nb/Fe and Fe_2Nb intermetallic was selected. The volume diffusivity as well as the grain boundary diffusivity was studied. The Fe_2Nb intermetallic simulated the phase, covering growing crystallites of Fe_xSi, the other materials could help to assess the Ge (Si) diffusivity along phase interfaces. Measured results were compared with relative literature values.
It was concluded that there are two possible rate controlling processes limiting the structure stability: (a) diffusion of Si (Ge) through the Nb-rich interfacial layer and (b) self-diffusion of Nb in the same phase. This means that Nb diffusion in the amorphous rest phase may not be the slowest (i.e. the rate-controlling) process determining the structure stability of FINEMET-type alloys as it is commonly believed.

Diffusion and Segregation in Nanocrystalline γ-Fe–Ni Alloy of a Two-Scale Microstructure

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Self- and solute diffusion in the nanocrystalline γ-Fe-40 wt.% Ni alloy has been studied. The nanomaterial has been produced by compacting and sintering the powders of Fe and Ni oxides. After pronounced grain growth during the sintering of the nano-material (from ~30 to ~100 nm) this nano-alloy pertains its small grain size after annealing up to 1100 K. Self-diffusion of Fe and Ni as well as Ag solute diffusion have been measured within an extended temperature interval from about 620 to 1100 K using the conventional radiotracer method and the serial sectioning technique.

In the material under investigation the individual nano-scale grains turned out to be clustered in micrometer-size agglomerates. Accordingly, the nanocrystalline GBs exist along with the inter-agglomerate boundaries. Diffusion in such a complex material presents an involved task and a Monte-Carlo simulation was used as a helpful tool to analyze the experimental penetration profiles.

The two different types of interfaces reveal qualitatively very different diffusion behavior: the diffusivity along the relaxed nanocrystalline GBs is similar to that in large-angle GBs in conventional coarse-grained materials, whereas the inter-agglomerate boundaries reveal considerably increased diffusivities and smaller activation enthalpies, which are likely to be related to a larger associated free volume of this type of boundaries. The nanocrystalline GBs probably attain their quasi-equilibrium state due to the above-mentioned grain growth during the applied sintering procedure. Performing GB diffusion experiments in practically all theoretically possible diffusion regimes, the Ag segregation to both types of internal interfaces was studied.

Anisotropic Characteristics of Hydrogen Permeation in Nano/Poly Crystalline-Nickel Membranes

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Hydrogen transport through nanocrystalline and polycrystalline bi-layer nickel membranes has been investigated by electrochemical hydrogen permeation. Each layer of a multilayer membrane has different characteristics of hydrogen permeation. When hydrogen is charged from opposite sides of the nano-Ni and poly-Ni composite membrane, the membrane shows anisotropic behavior for hydrogen permeation. Using this anisotropic behavior, one can manipulate hydrogen permeation through composite membranes. Traditional methods of analysis assume that samples are structurally homogeneous throughout the thickness, which is not true in our case. To explain anisotropic characteristics of hydrogen permeation in investigated membranes a Monte Carlo hydrogen permeation model for bi-layer membranes is proposed. This model is based on the assumption of different hydrogen diffusion and different solubility of hydrogen in the layers from which the membrane is composed. This approach allows simulating diffusion in a nano-Ni and poly-Ni bi-layer membrane for opposite directions of charging. The experimental data is in good qualitative agreement with the model.

Differential Scanning Calorimetry Analysis of the Formation of Nanometric Ni Silicide Thin Films on Si Substrate

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Silicides are widely used in microelectronics for contacts and interconnections. Nickel monosilicide, NiSi, is a promising candidate for ultimate CMOS transistors due to its low resistivity (15-20μΩcm) and low Si consumption. In the microelectronics process, silicides are formed by solid-state reaction between a metal film and a thick Si substrate. For Ni films deposited on crystalline Si substrates, the sequential formation of the three silicide phases is usually observed: Ni_2Si and NiSi at low temperatures (250°C-300°C) and $NiSi_2$ at around 750°C. NiSi is also a good candidate for metal gate, which might be obtained by reaction of Ni film and amorphous Si (α-Si). The tendency to shrink MOS devices, and thus the silicide thickness, requires a better understanding of the first stages of reaction for nanometric Ni silicide films.

In this paper, we report a study on the solid-state reaction between Ni and α-Si using differential scanning calorimetry (DSC). In order to obtain detectable DSC signals, samples are usually made of self-supported multilayers that generate more reacting materials and more interfaces where the interested reactions take place. However, the presence of multiple interfaces and/or the absence of substrate can modify the solid-state reaction mechanisms. In this study, we develop a procedure to analyse by DSC the formation of nanometric silicide thin film on a substrate. This procedure has been successfully used for acquiring DSC thermograms at different heating rates of 5 to 100°C/min for a 50-nm Ni film on a thick α-Si layer deposited on (100)Si. The DSC results indicate that the formation of Ni_2Si on α-Si follows a linear variation with time.

In-situ TEM Investigation of Diffusion of Nano-scale Liquid Pb Inclusions on Dislocations and in Bulk Aluminum

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Diffusion of nanosized liquid Pb inclusions in crystalline aluminum was investigated in-situ using TEM. The observations show that most Pb inclusions are trapped on dislocations and their motion is spatially confined in close proximity of the dislocations. They display 1D random motion along the dislocations and 2D chaotic vibrations in the transversal plane. The transverse vibrations of the inclusions originate from the dislocations operating like elastic strings. This is confirmed by the agreement between the rigidity of the dislocation found experimentally and an estimate based on a dislocation elastic model. This model is supported by observations of mutual repulsion of inclusions trapped on the same dislocation. Application of Einstein's equation that is valid for free random walks to determine the diffusion coefficients of trapped inclusions can lead to significant underestimation of their diffusivity. Instead, the diffusion coefficients were obtained using Smoluchowski's equation that takes into account the existence of a confining force field. Occasionally, the inclusions are seen to detach from the dislocations, and subsequently move in 3D free random walk. Their diffusion behavior obeys Einstein's equation. A comparison of the diffusion coefficients obtained for free and trapped inclusions indicates that the same underlying microscopic mechanism is responsible for the diffusion and that the influence from dislocations is minimal. The dependence of the diffusion coefficient on their size indicates that kinetic processes on the Pb/Al interface control their mobility.

Thermal stability of Li-doped metal-fullerene materials

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The recent explosion of the widespread research activity in the nanostructured materials has been fueled by great potential of their applicability. Because novel properties of the materials can be obtained through the synthesis of the nano- to micro-scaled self-organized structures, the considerable endeavor has been put into the understanding of mechanisms of their formation and evolution, and eventual into know-how of their fabrication. Composites consisting of organic and in-organic (or metallic) components are complex materials that often show higher-level patterned structures. One of the important issues is how to control their assembling towards forms exhibiting new functional capabilities.

In the present paper, fabrication and structural development of the metal-fullerene systems (mixed or sequenced) doped with Li or other dopants have been studied. The thin films of the hybrids were prepared in the MBE chambers either by co-deposition or by alternating deposition of components; doping of Li or other dopants was performed in vacuum. After doping the specimens were gradually annealed in the inert atmosphere (or vacuum) to induce re-arrangement of their structure and diffusion of the dopants. The effect of annealing on structural modification and mobility of dopants was monitored by several techniques including Neutron Depth Profiling, Rutherford Backscattering, micro-Raman Spectroscopy and Scanning Electron Microscopy. The results showed that the doped hybrid films exhibit (under heating at certain temperatures) specific phase transformation that results in considerable self-arrangement of the material.

Kinetic Demixing of Yttria-stabilized Zirconia

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Yttria-stabilized Zirconia (YSZ) is extensively used as a membrane material for oxygen ion conducting high temperature fuel cells (SOFC). Under operating conditions, it is exposed to an electrochemical potential gradient while being electronically short-circuited. While these conditions lead to the desired oxygen transport, they also cause a small cation transport towards the cathode side of the sample. If the cation sublattice consists of more than one component, and if the components show different mobilities, kinetic demixing can occur. Theoretical calculations show that kinetic demixing can have severe influence on the material's long term stability, especially for very thin membranes.

Demixing experiments were carried out on YSZ single crystals of 100µm thickness at temperatures of 1300°C with electric fields ($0.25V<U<0.5V$) as driving forces. Secondary Ion Mass Spectrometry (SIMS) was used for characterization of the surface-near demixing process. Our SIMS results show good evidence for the presence of kinetic demixing. Besides the demixing, strong morphological changes on the anode side took place. Pore formation in the vicinity of the anodic O2|Pt|YSZ triple phase boundary led to an increase of anodic exchange surface and there to a current rise. Morphology changes and pore formation are interpreted by means of theoretical models.

Scanning Probe Microscopy Study of Grain Boundary Migration in NiAl

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A *post-mortem* scanning probe microscopy (SPM) study of grain boundary (GB) migration in Ni-rich NiAl at 1400^0 C is presented. The migration of GBs during annealing is quantified using the SPM measurements of surface topography changes that it caused. Both GB migration and surface diffusion contribute to the observed topography changes. It is shown that the quantitative conclusions about the dynamics of grain boundary motion can be drawn from the study of surface topography in the vicinity of both individual migrated boundaries and migrated triple junctions. In the case of individual boundaries, the curvature of the blunted root of the grain boundary groove formed at original boundary position provides the information about the beginning of migration process. In the case of triple junctions that moved along one of three boundaries forming the junction, the variable width of the grain boundary groove allows to recover the dynamics of migration process. Using the Mullins model of surface diffusion controlled grain boundary grooving and its modifications we estimated that the grain boundary migration rate is 0.3 ± 0.05 μm/s. This is much higher than the average migration rate obtained by dividing the migrated distance by total annealing time. It is concluded that in the near-surface region the grain boundaries migrate in jerky, spasmodic fashion.

The Field Effect on the Skirt of Electrons at High Pressure Scanning Electrons Microscopy

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The high-pressure scanning electron microscope (HPSEM) allows the examination of specimens in a gaseous environment operating at pressures up to 300 Pa. This kind of microscope permits to annihilate the negative charge exes on the sample by the positive ions created after the pass of electrons beam in specimen chamber. These ions are directed toward the sample by the voltage applied on the wall of specimen chamber. The amount of created ions decreases at high vacuum conditions and consequently the voltage on the insulating sample can reach some kilo volts. Many instrumental parameters are directly related to the skirt and are discussed by different authors in the literature, as due to pressure, electrons beam voltage, working distance, and chemical nature of atom gas

In this paper we will present the field effect on the electrons boarding using Monte-Carlo simulation. The results show that the magnitude of field applied on the wall of specimen chamber of HPSEM does not affect the skirt of electrons, which increases when the beam of electrons is in front of voltage in the magnitude of that created on the insulated sample at high vacuum conditions.

Diffusion Measurements in Chromium-Manganese Steels by Means of Multiple Radiotracer Test

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The paper presents the application of multitracer method of diffusion measurement in Cr-Mn steels. Three types of steels were investigated: austenitic steels 3H13G18S2Ca, 5H17G17 as well as austenitic-ferritic steel 0H15G19. The serial sectioning technique was used to simultaneous evaluation of diffusion coefficients of radioisotopes of chromium ^{51}Cr, manganese ^{54}Mn and iron ^{59}Fe. All used isotopes emit γ radiation of high energy so the absorption of radiation in the material of the sample can be neglected. In this case the residual activity is proportional to total content of the radioisotope in the sample. Hence, in experimental procedure, not only the activity of the removed layer (differential method) was measured, but also the residual activity of the specimen after removing of the layer (integral method). In both cases the counting rate was counted using scintillation (NaJ(Tl)) counter. The artificial neural networks (ANN) were applied in data analysis. It was found that the diffusion rate of manganese is higher than that for iron and chromium. It explains partly the morphological structure of the scales formed on the steels studied, which are composed mainly of manganese compounds (MnO - in the outer layer, and $MnCr_2O_4$ spinel – in the intermediate region of the scale). The authors plan also to evaluate the diffusion coefficients of radioisotopes of ^{51}Cr, ^{54}Mn and ^{59}Fe in the scales compounds. The depletion of manganese close to the metal/scale interface causes the phase transformation from austenitic to ferritic structure, and decreases diffusion rate. On the base of the diffusion data, obtained at different temperatures, the activation energy of diffusion was estimated.

Reactive Diffusion in Olivine [$(Mg,Fe)_2SiO_4$]

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Olivine, $(Mg,Fe)_2SiO_4$, a greenish mineral, is of great significance to the earth and planetary sciences. Olivine is the first silicate condensate from the solar nebula and thus a major constituent of the earth and the terrestrial planets, as well as certain meteorites. Compositional gradients of Fe and Mg, which occupy the same octahedral position in the crystal lattice, are common. Diffusion modeling of compositional gradients in olivine provide information about timescales of geological processes, e.g. magma generation or cooling rates of rocks.

Point defect chemistry of olivine is well known, but the effect of moving boundaries or simultaneous reaction on diffusion has not yet been studied. Therefore we carried out evaporation experiments in a vacuum furnace ($2x10^{-6}$mbar) at a high temperature (1400°C), for this is the cleanest way of introducing a mobile interface in a refractory silicate or oxide. We used oriented, polished single crystals (X^{Mg}~0,9) and anneal durations were between 5 and 100 hours.

Olivine evaporates stoichiometrically, but the Fe-component evaporates more rapidly than the Mg-component, which leads to an enrichment of magnesium at the surface (X^{Mg}~0,99) and diffusion of iron from the inner parts of the crystal. Diffusion profiles have then been measured with an electron microprobe.

Our measured average evaporation rate was 0.3 µm/hr. Modelling the concentration profiles, we found that a compositionally dependent Fe-Mg interdiffusion coefficient of $D = 6{,}95 \text{ x } 10^{-15}$ m^2/s for $X^{Mg}=0.92$ provides a best fit of the observed profiles in all our runs. This is about 22 times faster than diffusion measured under static conditions. Currently, we are carrying out detailed microstructural characterization using electron back scatter diffraction and TEM to further quantify this interaction between a dynamically evolving microstructure and diffusion process.

Reactive Diffusion in Mo-Si System Above the Melting Point of Silicon

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The results of direct kinetic measurements and SEM observations on formation of silicide phases in Mo-Si system at temperatures 1400-1700°C are presented in the work.

It is established that a multilayer diffusive zone is formed on the molybdenum surface when it comes in contact with molten silicon, and simultaneously, the metal is dissolved in liquid silicon with formation of Si-$MoSi_2$ eutectic. As a consequence of diffusive processes occurring in opposite directions, the boundary between silicide diffusion zone and eutectic melt can move in different directions depending on the ratio of Si and Mo fluxes.

As SEM investigations of quenched samples have shown, the primary product observed is disilicide phase, which is formed in the bulk of liquid silicon as fine particles with characteristic size less than 1 μm. After the melt is saturated by disilicide, the process of $MoSi_2$ crystallites nucleation and their growth takes place. The latter proceeds up to complete consumption of silicon after which the whole silicide zone becomes compact and includes two disilicede layers as well as a thin intermediate Mo_5Si_3 layer.

Thus, the formation of $MoSi_2$ final product proceeds by two various mechanisms. Accordingly, two types of final product microstructures are formed: (i) a compact layer (usually showing columnar structure) by the reaction diffusion mechanism; and (ii) separated fine grains by crystallization in the volume of saturated Me-Si melt.

The formulated model of product formation allows to calculate the relative contributions of the two above-listed mechanisms of disilicide phase formation at various stages of interaction and to estimate the role each of them in the total process.

Phase Transformations during the Heating of Fe-Si-B Amorphous Alloys

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Phase transformations during the heating of Fe-Si-B amorphous alloys were investigated. The differential thermomagnetic analysis and X-ray method are used for the studies. The intervals of phase transformations are revealed, and the magnetic properties of phases are determined. The method of calculation of magnetic effects during the phase transformations, registered by differential technique is suggested.

The thermomagnetic curves of heating of the amorphous alloys Fe-Si-B are reversible if the temperature of heating is no more than 470°C. This leads to conclusion that Curie temperature is close to 410–420°C. Beginning from the temperature of 480°C the sharp irreversible increase of the magnetization of this alloys is registered at the thermomagnetic curve. The heating to 600°C and the consequent cooling down to room temperature has shown, that the irreversible increase of a magnetization registered in an interval of the temperatures 480–520°C, is not exhibited at the temperatures close to room temperature. The increase of the magnetization of this alloys in the temperature interval 480–520°C is the result of the crystallization.

The X-ray analysis carried out by us showed that after the heating to 500°C the alloy contains α-Fe and borides FeB and Fe_2B.

Using the experimental data that were obtained the specific magnetization of Fe-Si-B amorphous alloys were calculated.

The methods that are proposed in this work could be used in studying properties of amorphous ferromagnetic bands and in investigating the effects of different kinds of treatment on these properties.

Nonlinear Photo-diffusion in Amorphous Chalcogenide Multilayers

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Photo-stimulated interdiffusion was experimentally observed and was applied for optical recording purposes in several multilayered nanostructures such as Se/As_2S_3 [1], $As_{0,2}Se_{0,8}$/$As_{0,2}S_{0,8}$ [2], $Se_{0,8}Te_{0,2}$/$As_{0,06}Se_{0,94}$ [3], but the detailed mechanism is still not well understood. We have done some computer simulations of laser-stimulated diffusion in amorphous chalcogenide multilayers, based on the numerical solution of the Fick's second law, with the aim of better understanding of the peculiarities of the photodiffusion process. The calculations were carried out for a multilayer consisting of a wide and a narrow band gap material with an initially sharp interface illuminated with He-Ne laser light (λ = 0,63 μm). It is assumed, that initially the light is absorbed exclusively in the narrow band gap material. These conditions are typical for the first two mentioned types of multilayers. Theoretical considerations show that the effective diffusion coefficient has to be proportional to the amount of the absorbed light that correlates with the absorbtion distribution profile which is finally determined by the concentration profile. This resulted in the nonlinearity of the photo-diffusion and in qualitatively different profile with respect to the case of thermo-diffusion.

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Non-parabolic Shift of Phase Boundaries in Binary Systems with Restricted Solubility

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Computer simulations [1-2] were performed to study the interplay of the diffusion asymmetry (composition dependence of diffusion coefficient) and the phase separation tendency (chemical effect) on the kinetics of the interface shift during dissolution in a binary system. The sample consists of A and B atoms, the initial state is fully separated, and there is always a sharp gap in the interface due to the restricted miscibility. We have found that taking into account only the diffusion asymmetry the interface shift is not proportional to the square root of the time as would be expected from Fick's laws (see also [1]) but to t^{k_c}, where $0.5 < k_c < 1$ (deviation from the parabolic law). On the other hand, the consideration of the phase separation tendency compensates this "deviation" as well and as the mixing energy (V) increases the interface shift returns to the parabolic law ($k_c \approx 0.5$) [2]. Note that at very large V, k_c can be less than 0.5. It is worth mentioning, that this effect is a real "nano-effect", because after dissolving a certain number of layers (long time or macroscopic limit), the interface shift returns to the parabolic behaviour independently of the input parameters.
We have performed XPS based experiments on Ni/Au system which prove the above results.

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Wetting of GBs in Zn by Al-reach Solid Phase

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The critical role of interfaces, such as grain boundaries (GBs) or interphase boundaries (IBs), on the properties of materials is well known. In the last years, the phenomenon of interfacial wetting has become of great interest due to the fact that peculiar electrical and mechanical properties of materials can be caused by a wetting phase. Although the interfacial wetting by a liquid phase has been studied from the theoretical and experimental point of view, investigations on wetting by a solid phase are rather difficult to be found. In the present contribution, the occurrence of such a wetting has been studied in Zn bicrystals in contact with Al-reach phase and in Zn–5 wt.% Al polycrystalline alloys. The microstructure of the heat-treated samples has been investigated by optical microscopy. The composition of the phases present in the specimens has been determined by electron probe microanalysis. It has been observed that at temperature just below the eutectic temperature more than 50 % of the (Zn)/(Zn) GBs were coated (wetted) by a continuous layer of the (Al) solid solution. With decreasing temperature the contact angle becomes non-zero and the number of (Zn)/(Zn) GBs covered by this layer decreased. Just above the eutectoid temperature all (Al) precipitates at the (Zn)/(Zn) GBs exist as isolated particles. For the first time, the concept of grain boundary wetting by a solid layer has been observed experimentally. The financial support of Russian Foundation for Basic Research, German Federal Ministry for Education and Research, Deutsche Forschungsgemeinschaft, NATO and INTAS is acknowledged.

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Iron Diffusion Near Surface of Fe_3Si is Fast and Decays to Bulk Values within 3 nm

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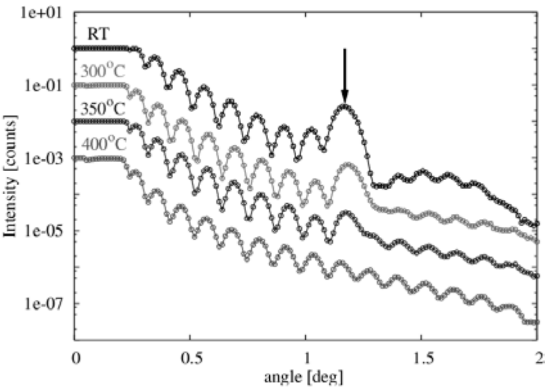
Nuclear resonant scattering (NRS) methods allow to perform measurement of elementary atomic jumps. A combination of NRS and grazing incidence geometry can be used as a very sensitive tool to investigate thin films or surface-regions. Fe_3Si with a stable $D0_3$ structure and a well known diffusion mechanism was chosen for this investigation.

An interesting task is the comparison of the diffusion in a near-surface layer and in a bulk crystal of Fe_3Si. To solve this task an Fe_3Si thin film was produced by annealing of an Fe/Si multilayer created by molecular beam epitaxy. The disappearing superstructure peak (arrow) shows transformation from multilayer into single layer structure at 400°C (see figure). The **bulk** diffusion coefficient in the single layer agrees with values from tracer and QMS measurements. The surface sensitivity of the method allows to fit a diffusion profile with gradually **enhanced** diffusivity in the **near-surface** region.



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Dynamics in an Iron Sub-monolayer

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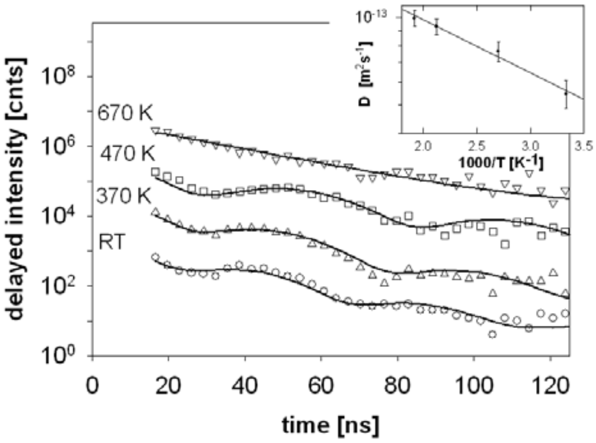
Electronic and dynamical properties of a sub-monolayer Fe film on a W(110) substrate have been investigated with nuclear resonance scattering in grazing-incidence geometry. This method combines the high brilliance of a third generation synchrotron source and the excellent characteristics of Mössbauer Spectroscopy and is best suited to study structural and magnetic properties of materials as well as dynamics on an atomistic scale. A relaxation model was used to explain the temperature dependence of the NRS spectra. The relaxation rates and diffusion coefficients have been calculated from the temperature dependence of the beat period (see figure).



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Degradation on the Division Surface of Phases: Superconductor / Ferrite During Sintering Process

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The processes on the phase division surface in the granular and the sandwich composites during the sintering were investigated. The matrix was a high temperature superconductor Bi (Pb) 2223 with Tc= 110^0C and the second phase was ferrite $NiFe_2O_4$ with Tc (Neel)=585ºC as grains with a diameter d~28 μm. The investigations were done using granular and sandwich composites sintered in different conditions of temperature and time. During the sintering process the phase degradation in the interface was observed. In order to analyze the degradation processes the following methods were used: scanning electron microscopy, XRD microanalysis and XRD phases analysis. Several new phases were identified. By solving the second Fick's law, for the diffusion from a sphere and the diffusion of flat front, the diffusion parameters were evaluated. The model of the phenomenon on phase division zone was elaborated.

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Advances in the Study of Diffusion Along Migrating Grain Boundaries

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Certain phase transformations in metallic alloys take place at migrating grain boundaries. *Discontinuous precipitation* (DP) is a typical example. DP involves the formation of a solute-depleted phase and a precipitate phase as a usually lamellar microstructure behind a grain boundary (GB) advancing into the supersaturated matrix. A discontinuous change in both the crystal orientation and the solute concentration of the parent phase across the moving reaction front (RF) characterize this kind of reaction. The DP reactions are controlled by diffusion along the migrating grain boundary. Kinetic studies of this reaction have recently led to reliable information on diffusivities along the GBs. This is of particular interest for systems and/or at temperatures where (radiotracer) diffusion data for stationary GBs are not/will not become available.

Analytical electron microscopy is a powerful technique to investigate the local composition changes accompanying the DP reaction. By means of this technique it was demonstrated that an abrupt change in the solute concentration occurs across the RF as well as that a concentration variation exists in the solute-depleted lamellae of the parent phase in a direction parallel to the RF. The local compositional analysis has allowed to remove existing discrepancies in the diffusivities obtained applying different models.

In the present contribution, a further step in the study of diffusion along migrating GBs in a discontinuous precipitated Cu–In alloy is reported. Using a VG HB-501 UX dedicated STEM, equipped with an energy-dispersive X-ray spectrometer, a small rectangular area (3 nm x 4 nm) including the RF was illuminated. For the first time, the concentration gradient *along the RF* of DP was measured experimentally.

Diffusion-controlled Coarsening with Noise

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The process of 3D diffusion-controlled coarsening, namely, the growth of large particles at the expense of small ones, is characterized by (1) time dependence average size and (2) particle size distributions (PSDs). The Lifshitz-Slezov-Wagner theory predicts, that average size changes with time as $<R> \sim t^{1/3}$, which gives a good agreement with experimental observations. But, experimentally obtained PSDs at the asymptotic stage of ripening are usually broader than those predicted by LSW-theory. “Noise” can be one of the reasons of such discrepancy. There are at least three possible sources of noise - scattering of diffusivities D in the vicinity of precipitates due to local structure inhomogeneities in the parent phase, scattering of surface tensions γ, and scattering of compositions (supersaturations Δ) in the vicinity of particles – local deviations from the mean-field level.

In our work the process of growth/shrinkage of precipitates had been investigated by taking into account a noise from different sources. We consider a noise of gaussian type consisting of many independent contributions with additive dispersions. The PSDs had been obtained by means of computer simulations for different values of noise.

Analysis of PSDs using parameters, which characterize a width, sharpness and slope of peak demonstrate that even for low level of noise a shape of PSD differs from one predicted by LSW.

Peculiarities of Precipitation of Intermediate Phase in Ternary Alloys

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In the binary systems the models of precipitation of intermediate phase predict the parabolic law of growth and constant concentration of component both in precipitate and its vicinity in parent phase. Such process in ternary alloy has qualitative distinction from binary one.

In our work the peculiarities of precipitation of intermediated phase in ternary alloys have been investigated for two cases: (1) the growth of spherical particles of quasi-binary intermediate phase $(CuNi)_3Sn_1$-type in supersaturated ternary solution of component C in binary alloy AB and (2) the growth of stoichiometric ternary phase in supersaturated weak solution based on one of the components. In the first case at the initial stage a non-parabolic growth of particle has been observed. At the same time a composition in the precipitate changes with time approaching the some asymptotic value, which is determined by the relationship of diffusion parameters. In the second case we obtain a “phase transformation” of shape. The growth of precipitate in the form of spherical particle becomes impossible for the sizes exceeding certain critical size, instead a two-phase zone has to appear and to grow.

Interaction of Phase Transformation and Deformation Process During Hot Deformation of 0.16%C Steel

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The present work has been inspired by previous researches performed on Cu-Ti [1] and CuNiSiMg [2] alloys undergoing multi-step phase transformation during high temperature deformation. There is a considerable amount of experimental evidence that interaction of hot deformation and complex phase transformation that includes discontinuous precipitation, leads to flow localization and shear bands development. Non-uniform deformation accelerates discontinuous precipitation within shear bands and dynamic coarsening of precipitates. In result of reduced precipitation hardening within SB's an intense flow softening was noted on flow stress curves at larger strains. Since the structure of these alloys obtained due to discontinuous phase transformation is morphologically similar to a pearlite structure in steels, one may assume that also austenite (γ) to ferrite (α) and pearlite (P) transformation in steel may also lead to localized flow under hot deformations conditions. Moreover, dynamic recrystallization being enhanced by strain localization and $\gamma \Rightarrow \alpha$ transformation may result in localized distribution of ferrite and perlite within the material structure after cooling the sample within $\gamma \Rightarrow \alpha$+P range.

There is a lack of data, which are referred to specific features of the phase transformation $\gamma \Rightarrow \alpha$+P under dynamic conditions. Therefore, the presented work concerns a study of the effect of hot deformation process within the temperature range corresponding to the $\gamma \Rightarrow \alpha$+P transformation on the carbon steel structure developed due to static and dynamic structural processes.

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Sb Diffusion in Amorphous Si Thin Film

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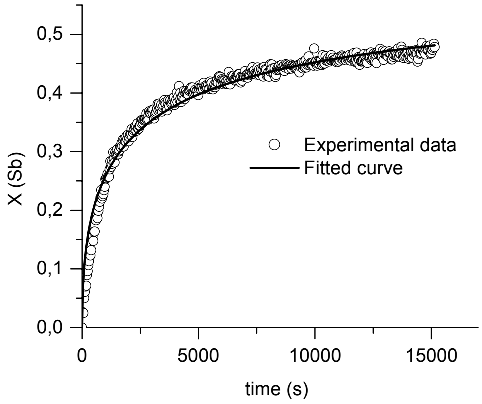
Antimony surface kinetic measurements were carried out in Sb/Si bilayers in the temperature range of 600 - 800K using Auger electron spectroscopy. Sb (20 nm) layers covered by amorphous Si (20 or 30 nm) layers were DC magnetron sputtered onto silicon oxide substrates. During the heat treatment time evolution of Sb and Si Auger signals were monitored in situ in order to determine the surface fraction of Sb. Transmission electron microscopy investigations as well as computer simulations of the system have been performed and using the calculated kinetic curves, diffusivities, segregation parameters and solubility (Sb in amorphous Si) can be determined.



Typical time evolution of Sb surface fraction

Hysteresis in the Process of Nucleation and Phase Separation in an Ensemble of Small Isolated Particles

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It is known that a system quenched into the two-phase region separates via nucleation and growth of the new phase nuclei. Hereby it is found that the boundaries for first order phase transitions, in nano-size systems (in our case in particles with a diameter in the range 1-100 nm) deviate from the macroscopic ones.

The corresponding dynamics of nucleation, crossover phenomenon and separation kinetics in nanopowders (nanosized system) is not well understood yet.

The objective of present work was to describe the separation kinetics (unsteady-state kinetics of nucleation, growth and separation) in nanopowder related to:

(i) the finite (non-negligible) depletion of parent phase in nanoparticles even at the nucleation stage;

(ii) finite rates of temperature changes during the annealing and heating;

(iii) the finite size of the system.

The conservation of matter in the parent phase, which leads to constraints on nucleation and growth of a new phase, is taken into account. The well-founded specific peculiarity of first order phase transitions in nanomaterials: hysteresis, is demonstrated. As the size of a system (at other parameters fixed) and/or as the rate of temperature changes (at other parameters fixed) and/or as interphase tension decrease, the hysteresis loop narrows showing tendency to disappearance. The model predictions are demonstrated for an example model of a system with general hypothetical properties.

Anelastic Relaxation due to Diffusional Jumps of Carbon Atoms in $D0_3$ Ordered Alloys.

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Interstitial atom diffusional jumps under applied stress cause an anelastic relaxation in metals known as the Snoek peak. Carbon Snoek relaxation in α-Fe [1] and dilute iron [2] is known about fifty years while this effect in high alloy Fe-based compositions and intermetallic compounds is less studied: 1) carbon–solute atoms and 2) carbon–vacancy interaction, and 3) solute atoms ordering make the Snoek effect more complex and more difficult for interpretation.

We have studied (internal friction, TEM, X-ray, DSC) and analysed influence of these parameters (solute atoms, vacancy, ordering) on the relaxation caused by carbon atom diffusion in a few Fe-based alloys with composition close to Fe_3X: Fe-25%Al, Fe-25%Al-(Ti,Nb), (Fe,Cr)-25%Al, Fe-25%(Al+Si), Fe-25%(Al+Co). Carbon–solute atoms interaction significantly change the Snoek-type relaxation parameters as compared with α-Fe (activation energy and relaxation strength), while carbon–vacancy interaction can lead to new, so-called X-relaxation [3] in compositions with high vacancy concentration.

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The Influence of Element Thickness on the Zinc Layers on Iron Substrate

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Technology of the hot-dip zinc galvanizing requires precision in controlling parameters which influence interdiffusion of zinc and iron. The main parameters in this case are chemical composition and temperature of zinc bath. In industrial practice also size of elements and time of immersion are of significant importance.

Literature review shows that the influence of chemical composition and temperature on galvanizing process is discussed in many papers. However, only few of them describe the influence of element size on interdiffusion rate of zinc and iron. On the other hand, this phenomenon can be of primary importance for the microstructure and thickness of zinc layers due to resulting temperature gradients.

The paper presents the results of studies of microstructure description and thickness of layers obtained in samples of systematically varied thickness for two types of steel substrates. A conclusion has been drawn that the size of elements significantly modifies the conditions of zinc layer deposition during the hot-dip zinc galvanizing.

Calculations of Diffusion Paths in Ternary Systems using Effective Interdiffusion Coefficients

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Diffusion paths in ternary systems are generally nonlinear functions of concentration and their description is one of the most interesting problems in interdiffusion studies. It was shown recently [1] that the diffusion path (more exactly, the derivative of it) is directly related to the effective interdiffusion coefficients of the diffusing components in ternary systems. But using this relationship for calculation of diffusion paths in ternary systems meets sometimes difficulties connected with singularities of effective coefficients at zero-flux planes and at zero concentration gradient points.

The possibilities for practical use of effective interdiffusion coefficients of components for calculation of diffusion paths in ternary systems are analysed. It is shown that infinite values of interdiffusion coefficients at zero concentration gradient points do not affect remarkably the accuracy of calculation in the case of correct choice of variables. At zero-flux planes where the respective effective interdiffusion coefficient is equal to zero no calculation problem arises as zero-flux planes can occur evidently only for one of the components at the same time.

The results of calculation of diffusion paths for diffusion couples in the ternary systems Cu-Fe-Ni and Co-Fe-Ni using respective effective interdiffusion coefficients are presented. These results demonstrate a good accuracy of such kind of calculations even in the case of very strong deviation from linearity of diffusion path (the system Cu-Fe-Ni).

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Surface Chemical Reactions in Processes of Diffusion Mass Transfer

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The phenomenological theory for describing high-temperature interaction between metal and rarefied gaseous medium has been developed. The theory is based on postulate of duplex contact layer at the interface (with relative thickness 2δ) where the processes of gaseous component migration and chemical reactions occur. The non-stationary conditions of mass transport. The wide spectrum of boundary diffusion tasks on the short and prolonged time bases, namely to describe the kinetics of diffusant accumulation at the neighbourhood of interface. Partial aggrement of the suggested model is illustrated by the description of the kinetic of gaseous saturation of metal (nitriding and borating) at the rarefied medium. In order to reveal diffusion setting one of the offered boundary condition, which contains two components: derivative of diffusant concentration function with respect to coordinate and time were taken into consideration.The derived equations describe the time dependence of change of surface concentration of gaseous component, the kinetics of its accumulation owing to chemical reaction, the specimen mass transport owing to both the diffusive impurity solving and the chemical interaction. The role of temperature is estimated.

Application of Diffusion Couple Method on Slip Casting of High Solid Content Alumina-toughened Zirconia Nano-composite

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Application of the diffusion couple method, including the set-up of the experimental equipment for measuring the diffusion coefficient of the liquid during the formation and solidification of a green body by slip casting into a porous mold is presented. On the basis of the generalized theory of diffusion, a general mathematical model of the formation and solidification process, taking into account transfer of the liquid phase due to concentration gradient was elaborated. In order to determine the diffusion coefficient conditions were chosen, under which grad T (temperature) and grad P (pressure) are zero. This simplifies the description of the liquid transfer in terms of concentration diffusion. An experimental work was done on phenomenological process of the transfer of the liquid though a ceramic suspension. The value of the diffusion coefficient of the liquid was determined through the suspension-body system, composed of nano particle-sized Alumina-toughened zirconia. The diffusion coefficient was found to be independent of the concentration of the liquid.

Nitriding Kinetics of Iron-Based Alloys

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Nitriding of iron-based alloys leads to considerable improvement of the mechanical properties. If Fe-Cr alloys are nitrided two phases develop within the diffusion zone; ferrite with nitrogen dissolved and located on the octahedral sites, and CrN.

To describe the evolution of the thickness of the nitrided layers a numerical model was developed that has as important (fit) parameters: the surface nitrogen content, the solubility product of chromium and nitrogen dissolved in the ferrite matrix and a parameter defining the composition of the precipitated chromium nitride. Fitting of the model to the experimental data demonstrated for the first time that mobile excess nitrogen is present in the nitrided zone and considerably influences the nitriding rate. Excess nitrogen can occur as dissolved nitrogen, by the presence of CrN precipitate misfit-strain fields, and as adsorbed at interfaces between the submicroscopical precipitates and the matrix. In nitrided layers of Fe-Cr alloys a discontinuous transformation mechanism takes place, where chromium nitride and ferrite lamellae are formed. This coarsening of the precipitates is correlated with relaxation of the long-range misfit strain fields, and excess nitrogen cannot remain in a dissolved state.

Transmission electron microscopical investigations showed for the first time that even in discontinuously transformed areas, within the ferrite lamellae fine chromium nitride precipitates could be observed. This result is consistent with the presence of both mobile and immobile excess nitrogen within nitrided zones.

Simulation of Interstitial Atom Diffusion in fcc and bcc Metals with Point Defects

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This work is devoted to simulation of interstitial atom diffusion in fcc and bcc metals with point defects. The suggested approach assumes, that point defects can alter the surrounding of atom configuration and consequently the local magnitude of the activation barrier of the jump of interstitial atom. In a previous study we to considered interstitial-defect interactions and found that those interactions influenced sufficiently on diffusivities. In the present study we used the molecular static method to model the activation barrier set for different configurations interstitial atom – vacancy. Knowing the activation barriers, it is possible to calculate the rate of jump, and the Monte Carlo method, it is possible to model the interstitial atom migration. In the present study the variation of the interstitial atom diffusion coefficient with temperature was computed. In particular, the calculations were done for the systems iron-carbon and nickel-carbon. The simulation showed that within certain condition the acceleration of interstitial atom diffusion took place.

3D Monte-Carlo Model of Deposition and Grain Growth in Thin Films

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It is well known that under deposition of polycrystalline thin film the average lateral grain size is nearly the same as the film thickness. It means that the very process of deposition helps larger grains to grow (in lateral directions) at the extent of smaller grains. So, if the rate of the atom deposition is constant the lateral grain growth rate is linear. Recently simple semi-phenomenological model of this process (called FDGG – flux-driven grain growth) have been proposed by K.N.Tu, A.M.Gusak, I.V.Sobchenko (Phys.Rev.B, 2003, 67, 24-5408). Arguments of this simple model were mainly of geometrical nature without detailed account of inter-atomic interactions. Main idea was that the deposited adatom can choose what "host" grain to join, and usually chooses the larger one. It should lead to "mushroom effect" – overlapping of smaller grains by larger grains. Now we try to build up some atomistic model of FDGG.

Our Monte-Carlo model is a generalization of the common known Potts model of grain growth. Standard Potts model takes into account only non-diffusive atoms redistribution between neighboring grains. We have developed 3D kinetic Monte-Carlo model which takes into account deposition of adatoms and their diffusion on a substrate, nucleation and growth of grains, migration of grainboundaries, surface diffusion at the "top" grain surface. Our simulation proves that the lateral grain growth rate is linear, at least in certain range of deposition fluxes.

Diffusion Measurements of ^{67}Ga in Polycrystalline Magnesium

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Gallium grain boundary (GB) diffusion in polycrystalline magnesium was investigated by radiotracer residual activity technique using ^{67}Ga isotope. The diffusion measurements were carried out under conditions of Harrison's B-type kinetic in temperature range 639 – 872 K. An approximate evaluation procedure was used to calculate both volume diffusion coefficient D_v and GB diffusivity $P = s\delta D_\mathrm{b}$ (s is the segregation factor, δ the GB width and D_b the GB diffusion coefficient). The obtained results showed the following linear Arrhenius relationships:

$D_\mathrm{v} = 1.2 \times 10^{-4} \times \exp(-134.3\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{m^2\ s^{-1}}$

and

$P = 3.8 \times 10^{-9} \times \exp(-94.9\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{m^3\ s^{-1}}$,

where R is universal gas constant and T is the temperature. The obtained results were compared with literature data on Mg self-diffusion and with In impurity diffusion in magnesium.

Structural and Transport Properties of $La_{1-x}Sr_xCo_{1-y-z}Fe_yNi_zO_{3-\delta}$ Perovskite

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Among possible new candidates for IT–SOFC cathode (IT – intermediate temperature), materials from (La, Sr)(Co, Fe, Ni)O_3 system with perovskite structure seem to be particularly interesting, because of their high mixed ionic – electronic conductivity, sufficient catalytic activity towards reduction of oxygen, chemical stability and appropriate thermal expansion coefficient.

In this work we summarize studies on the influence of chemical composition and sintering conditions on the structural and electrical properties of $La_{1-x}Sr_xCo_{1-y-z}Fe_yNi_zO_{3-\delta}$. All the samples with different chemical composition were obtained by sintering precursors obtained by citric acid method. All the samples were characterized at RT by X – Ray diffraction technique followed by Rietveld method analysis, which revealed distorted perowskite structure. Charge state and local structure of Fe ions surroundings in selected samples were analyzed by moessbauer spectroscopy. Transport properties were characterized by a electrical conductivity (4-probe DC) and thermoelectric power (dynamic technique in variable temperature gradient) in the 77 – 1077K temperature range.

The results of the measurements suggest that $La_{1-x}Sr_xCo_{1-y-z}Fe_yNi_zO_{3-\delta}$ possess attractive properties as a possible cathode material for IT–SOFC, which can be substantially improved by optimization of the chemical composition of the material.

Lithium Diffusion in $LiMn_yFe_{1-y}PO_4$ Cathode Material

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Lithium iron phosphate and other olivine type compounds have recently emerged as a group of the most promising cathode materials for Li – ion cells [1]. Extraction of lithium from $LiFePO_4$ in the charging process of a lithium battery leads to coexistence of two phases: one with unchanged initial composition and the other with close to zero lithium content. Substitution of Fe with Mn, yielding $LiMn_yFe_{1-y}PO_4$ compound substantially changes the nature of the lithium extraction process [2]. For some compositions y the initial ($x = 1$ down to y) delithiation commences according deintercalation process, what means that a single phase cathode material with gradually falling lithium content is observed:

$$LiMn_yFe_{1-y}PO_4 - xLi^+ - xe^- \rightarrow Li_{1-x}Mn_yFe_{1-y}PO_4.$$

Further lithium extraction ($0 < 1-x < y$) accompanied by 0,7V voltage rise in the charge curve leads to two phase system:

$$Li_yMn_yFe_{1-y}PO_4 - xLi^+ - xe^- \rightarrow \ x/y\ Mn_yFe_{1-y}PO_4 \ + (y-x)/y\ Li_yMn_yFe_{1-y}PO_4.$$

Structural studies (XRD, ^{57}Fe moessbauer spectroscopy) and lithium diffusion measurements (by GITT method in lithium cells) were performed on deintercalated $Li_xMn_yFe_{1-y}PO_4$ samples. Within the potential jump region a change of charge transport mechanism and lithium diffusivity is noted, pointing to electronic properties as the decisive factor determining the actual delithiation mechanism.

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Failure Mechanism and an Estimating Method for Remainder Life of Pipe Elbow of Ethylene Cracking Furnace

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In this paper, the reasons and the mechanism of the failure of the pipe elbow of ethylene cracking furnace, which is made of ZG4Cr25Ni35WNb, are investigated. It was found that the original defects, microscopic degradation, carburization, oxidation, thermo-stress cycles and abrasion due to airflow are the main reasons for the failure of the pipe elbow. A new method, which can be used to calculate the remainder life of the pipe elbow by combining the Larson-Miller extrapolation parameter with the iterative algorithm, is presented. The method can be used to evaluate the equipment working at high temperature and high pressure, especially the equipment for oil and chemical plants.

3D-simulation of Void Formation, Growth and Migration Under Electromigration

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Void formation under electromigration (EM) - one of the main failure mechanisms in microelectronics – still remains not well understood. We are investigating the void nucleation at the copper surface, its growth, shape evolution, migration, interaction with grain boundaries in bamboo structure, coalescence.

Results of 3D kinetic Monte Carlo simulation will be presented. Only surface migration is simulated (bulk diffusion frozen). Atomic jumps along free surface of void are simulated according to Glauber algorithm with taking electron wind into account. Local redistribution of electric current and corresponding drift force is being recalculated after each jump.

Diffusion Analysis of Metallic Coatings on 9wt% Steel for Application in High Temperature Environments.

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In order for a coating to prevent high temperature corrosion, protective elements such as chromium, silicon or aluminium must be maintained above critical levels at the surface of components. Over the lifetime of a component/ coating system diffusion into the substrate and consumption of the elements via oxidation may reduce the levels of these elements leading to breakaway oxidation. Coating /substrate interdiffusion is one of the principle causes for loss of integrity of the coatings. This project was designed to study the interdiffusion behaviour of selected coating systems using the generalised darken Method (GDM).

Interdiffusion problems have been studied both in the closed and open systems. We shall discuss the issues of interdiffusion and consider the suitability of the GDM to predict the thermal stability of real coating systems.

Microstructure characterization of scales on AISI 316L stainless steel exposed to air at 900°C

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Elements of chemical installations made of 316L austenitic steel in industrial practice are frequently exposed to temperature reaching 900°C. Examination of the oxidation kinetics at such temperature in dry air was the aim of this work. Oxide scale spallation by conventional microthermogravimetry and Differential Scanning Calorimetry was confirmed. Secondary Ion Mass Spectroscopy was used to verify chemical composition of oxides and subsurface depletion zone. Scale morphology was revealed using Scanning Electron Microscope, Figure 1. Additionally, surface roughness analysis and nanohardness test was conducted.

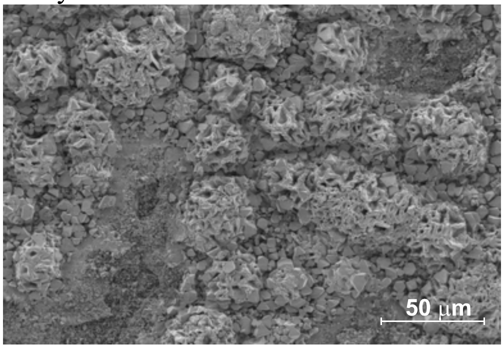

Figure 1. Surface of AISI 316L stainless steel after exposure in dry air at 900ºC. Oxides and the spalled regions, SEM image

Selective Etching of Phases and Structural Components in Duplex Stainless Steels”

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Microstructural complexity and constantly growing commercial importance of duplex stainless steels caused considerable development of many etching techniques to reveal general structure and distinction of each phases. Electrolytical technique assures selective etching of phases using the same solution of electrolyte only by changing the applied potential of electrolysis, what acts these methods preferential to conventional chemical methods of revealing microstructure.

With purpose to preferential color etch of ferrite in duplex stainless steels, 20% NaOH and 10 N KOH aqueous solutions were used. In case of samples without heat treatment, it has been found that sufficient revealing of microstructure was taking place at comparativety short times of etching (20% NaOH: 3 V, > 3 s; 10 N KOH: 2-5 V, > 5 s). Besides at enough long times of etching, revealing of grain boundaries in the ferrite phase was also possible (20% NaOH: 3 V, > 90 s; 10 N KOH: 5 V, > 30 s). Electrolytical etching in hydroxide solutions may also be used to reveal sigma phase in 2205 duplex stainless steel microstructure. Particularly useful in revealing grain boundaries were acidic reagents. The best results in revealing grain boundaries using 60%HNO_3/40%H_2O was obtained at relatively short times of etching (5 V, 5 s; 10 V, 1-3 s). Very similar results have been obtained using aqueous 10% oxalic acid, at 3 V potential of electrolysis, optimum circumstances of etching process have been found for times 20-90 s. The electrolytic 5% H_2SO_4 etch revealed grain boundaries fully and uniformly without bringing up the annealing twins.