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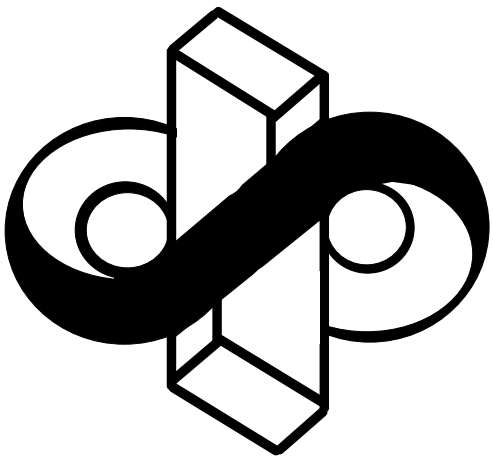

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The correlation between GB energy, crystallography and chemical composition in NiAl

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Severe intergranular brittleness at low temperatures hinders engineering applications of NiAl, which otherwise exhibits an excellent combination of low density, high strength, and high corrosion resistance at elevated temperatures. In our research we explored the possibility to improve the low-temperature mechanical properties of NiAl using the grain boundary (GB) engineering approach.

The physical parameter that determines the GB strength in brittle materials is GB energy. It depends on the alloy composition as well as on the geometry of GB. The latter can be described by five *macroscopic degrees of freedom* (DOFs). The goal of this research was to establish a correlation between the GB energy and its geometrical DOFs.

The atomic force microscopy (AFM) and electron back-scatter diffraction (EBSD) were employed for characterization of GB energy and crystallography. The GB energy was determined relatively to the surface energy and was assessed through the dihedral angle of the groove, which is formed during thermal annealing. Three out of the five macroscopic DOFs (the misorientational) were measured by EBSD analyses at both sides of the GB and the other two DOFs (GB plane inclination) were determined by the serial sectioning technique.

The parameters of 43 GBs were measured for the bulk composition of 40.3±0.3 % at. Al. The relative GB energies varied in a wide range of 0.2-1. The wide range of GB energies indicates that there is a great potential for improving mechanical properties of NiAl using the GB engineering approach. The research results indicate that there is a significant extent of surface anisotropy for the Al-rich compositions. This anisotropy did not allow us to determine the GB energy for these compositions. Also, it has been found that that the mixed tilt/twist large-angle GBs exhibited particularly low values of GB energy. An additional conclusion of this research is that twist GBs are generally more energetic than their tilt counterparts for the fixed misorientation angle.

No obvious correlation between the parameter Σ (reciprocal density of coincident sites) and the GB energy was established. The results of the research were discussed in terms of geometry of the crystallographic planes that comprise the GBs. Finally, a novel technique that enables to trace the process of grain boundary migration was developed.

Large Ag radiotracer diffusion and segregation in γ-FeNi-nanocrystalline alloy of Bi-modal interface structure

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A comprehensive investigation of Ag bulk and grain boundary (GB) solute diffusion in coarse-grained (grain size of several hundred of micrometers) and in the well-compacted and sintered nanocrystalline (grain size 80 to 100 nm) γ-FeNi alloy (40 wt.% Ni) was performed. Due to pronounced agglomeration of the nano-material – individual nano-scaled grains turned out to be arranged in micrometer-sized clusters or agglomerates – two types of internal interfaces with different length scales and diffusion characteristics (the boundaries between the nano-grains and between the agglomerates of these nanocrystallites) act as short-circuit diffusion paths in that case. A systematics of grain boundary diffusion in such bimodal structure is outlined in dependence on the given diffusion regime. The well-known Harrison's kinetic regimes of grain boundary diffusion in unimodal polycrystals had to be reanalyzed for a proper interpretation of the sophisticated experimental profiles. The mathematical apparatus to extract diffusivities of nanocrystalline and inter-agglomerate boundaries from the multi-stage experimental profiles is elaborated. A Monte-Carlo study of GB diffusion in the agglomerated nanocrystalline material was performed to figure out practical limits of the kinetic regimes in question. Grain boundary diffusion measurements of Ag solute diffusion in coarse-grained and nanocrystalline γ-FeNi alloy in different kinetic regimes, i.e. measurements of D_{gb}^{Ag} and $P^{Ag} = s\delta D_{gb}^{Ag}$, allowed to establish the segregation behavior of Ag in this alloy.

The absolute values and the Arrhenius parameters of Ag diffusion along the nanocrystalline boundaries in the nano-γ-FeNi alloy are similar to the corresponding GB diffusivities in coarse-grained polycrystalline γ-FeNi. The activation enthalpy of diffusion along the inter-agglomerate boundaries turned out to be notably smaller and the absolute diffusivities larger by two to three orders of magnitude than the corresponding diffusion values via the nano-boundaries.

New approach to a description of diffusion properties of nonequilibrium grain boundaries

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New approach to the description of diffusion in equilibrium and nonequilibrium general grain boundary is developed. It is supposed that vacancy in the irregular atomic structure of grain boundary is unstable and delicalize due to relaxational displacements of atoms. Variation of the free energy of a grain boundary – crystal system upon the transition of vacancies from the bulk of grains into grain boundaries is analyzed and equilibrium excess volume of grain boundary υ^* is calculated. As an elementary act of grain boundary self-diffusion, the formation of a metastable localized grain boundary vacancy is considered. Expressions for the activation energy and diffusion coefficient in equilibrium $(\upsilon = \upsilon^*)$ and nonequilibrium $(\upsilon \neq \upsilon^*)$ grain boundaries have been obtained. Mechanisms of nonequilibrium excess volume formation during plastic deformation and kinetics of recovery of nonequilibrium grain boundary diffusional properties are considered.

Diffusion-induced interfacial effects in nanostructures

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Interdiffusion in nano-structured materials (NSM) at relatively low temperatures occurs mainly inside the wide network of grain boundaries (GBs), which are simultaneously short-circuit diffusion paths and sources and sinks of vacancies. This peculiarity provides the accompanying diffusion-induced interfacial phenomena such as GB Kirkendall and Frenkel effects and decay of multi-layered nano-structures, which. are crucial for stability of NSM and their functional characteristics.

GB Kirkendall effect was analyzed theoretically and measured experimentally on diffusion couples composed from nano-dispersed Cu and Ni layers compacted from nano-powders of 8-12 nm sizes. GB Kirkendall shift obeys the kinetic law $\Delta x_b \sim t$ ¾. The inequality of GB Cu and Ni partial diffusion coefficients was estimated as $(D_{bCu} - D_{bNi}) / D_b \approx 0.5$. The insertion or elimination of atomic planes inside interfaces at GB Kirkendall effect leads to stress generation in the grain interior. Different forms of stress relaxation were studied in experiments on lateral interdiffusion in nano-structured Cu-Ni and Ag-Au thin film couples with overlap between two different films.

GB Frenkel effect consists in pore forming along GBs from extra vacancies produced by GB interdiffusion in component with higher diffusivity. Under tensile stresses extra vacancies coagulate in micro-pores decorating GBs. Porous zone spreads from overlap line on kinetic law $l_p \sim t$ ¼, demonstrating that pore formation is controlled by GB interdiffusion.

Interdiffusion in binary multi-layered systems with alternating A and B nano-layers is accompanied by decay of layered structure and its transformation into isomer globular one. The model of this process based on interdiffusion along migrating GBs and interfaces between different layers with subsequent solution formation behind moving boundaries was proposed and driving forces of these processes were analyzed. The kinetics of low-temperature homogenization and decay of layered structure was studied on binary system Ni-Cr and discussed in terms of proposed model.

Grain boundary recovery and its relation to grain boundary diffusion in nanocrystals

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Most of the methods applied to fabricate nanocrystalline materials generate non-equilibrium grain boundary structures. This is proved by observations of internal strains and free volumes in as-prepared nanocrystals and of energy release during DCS experiments prior to a significant grain growth. During annealing, including diffusion experiments with nanocrystals, non-equilibrium grain boundaries evolve toward equilibrium. This process referred to as a grain boundary recovery is very important for the stability of nanocrystalline structure and for the kinetic properties of polycrystals.

In the present paper the results on the studies of recovery in grain boundaries having different types of non-equilibrium structure are reported. First type structures are characterized by the presence of extrinsic grain boundary dislocations (EGBDs) that is common for submicrocrystalline metals prepared by plastic deformation techniques. These structures relax by the accommodation of EGBDs that involves an escape of the dislocations from grain boundaries through junctions. Mechanisms for the annealing of gliding and sessile EGBDs are proposed and related kinetics are calculated. Structures of the second type are characterized by a non-optimized rigid-body translation state of grain boundaries and are common for nanocrystals prepared by crystallization from the melt or amorphous state. These structures have also been observed during molecular dynamics simulations. A mechanism for the diffusion controlled optimization of rigid-body translations is proposed and corresponding relaxation time is calculated. This mechanism operates at grain sizes less than about 10 nm, while for larger grain sizes relaxation occurs by the formation of triple line dislocations.

If one assumes that the instantaneous value of grain boundary diffusion coefficient is given by Borisov's relation with an energetic term equal to the excess energy of non-equilibrium boundaries, the grain boundary recovery occurring during diffusion annealing of as-prepared nanocrystals can significantly influence the experimental values of the diffusion coefficient. A solution to the diffusion equation with variable diffusion coefficient is obtained for diffusion in regime "C". On the basis of this solution and the data on the kinetics of grain boundary recovery the existing experimental data on the grain boundary diffusion coefficient in nanocrystals are analyzed.

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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. By the use of the model the average rate of the crack growth was estimated.

Dynamics of grain groove close to wetting condition

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We consider the problem of surface groove growth based on the classical Mullins's physical assumptions. Tangent angle - arc length variables are used instead of traditional Cartesian coordinates in formulated mathematical problem. Such parameterization allows to deal with , and to describe non-single valuated π the complete range of dihedral angles from 0 to surface profile. Numerical analysis of self-similar solutions of the problem shows that the non-zero flux of atoms along the grain boundary at triple junction (as in the case of experiments with wetting transition) gives rise to non-single valued surface profile and can destroy the self-similar solution. This leads to the birth of pores on the grain boundary under free bicrystal's surface. Critical conditions for pores generation and existing of self-similar solution are presented.

Deformation and pressure dependencies of amorphized and nanocrystalline structure formation in Ti-Ni alloys subjected to high pressure torsion

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Structure formation in the course of high-pressure torsion (HPT) of Ti–50.0 wt. % Ni (1), Ti–50.7 wt. % Ni (2) and Ti–47 wt. % Ni–3 wt. % Fe (3) shape memory alloys after N = 1, 3, 5, 10, and 15 revolutions at P = 4,6 and 8 GPa pressures on the samples of 3 mm in diameter and 0,2 mm in thickness was studied using X-ray diffraction and transmission electron microscopy (TEM) methods. X-ray line width B increases at great extent as HPT strain increases, and reaches a certain limit, which is the same for all three alloys. It means that finally, after HPT in 10 to 15 revolutions all studied alloys obtain the same structure. However, the kinetics of B change in different alloys is different. Namely, the stabilization of B is reached at N = 3 or 5 to 10 in alloys 1, 2 and 3, correspondingly. TEM study confirms that the kinetics of the formation of same final structure is different in different alloys. Finally, at rather large strain the amorphized structure forms. In Alloy 1, after HPT with N =5 at P = 4GPa the nanocrystalline and amorphized structure is observed. It contains intermittent nanocrystalline and amorphized areas. The amorphized structure occupies large continuous fields in Alloy 1. The gaps between these fields contain mixed structures. The amorphized fields and regions contain also finally dispersed nanocrystalline inclusions. In Alloy 2, after HPT with N = 5 at P = 4GPa, mixed nanocrystalline and amorphized structures are observed in approximately equal fractions. In Alloy 3, in the same conditions only nanocrystalline structure is observed together with traces of strain-hardened substructure. The structure of all three alloys after HPT with N = 10 at P = 4 GPa, is the amorphized one containing nanocrystalline inclusions. Thus, a tendency to form an amorphized structure increases in the sequence from Alloy 3 to Alloy 2 and Alloy 1. It seems that it depends on relative positions of M_S and deformation temperatures. Change of the pressure from 4 to 8 GPa at HPT with N = 5 leads to a suppression of the amorphized structure formation in Alloy 1. The amorphized areas become narrower and nanocrystalline structure fraction considerably increases. From place to place, pre-nanocrystalline strain-hardened dislocation substructure is observed. In the Alloy 2, after HPT with N = 5 the increase of the pressure from 4 to 8 GPa reveals the same tendency as for the Alloy 1 and after HPT under 8 GPa, only nanocrystalline structure plus strain-hardened dislocation substructure are observed. In Alloy 3, the tendency manifests itself in a transition from the completely nanocrystalline structure after HPT under 4GPa to the mixed nanocrystalline structure plus strain-hardened dislocation substructure after HPT under 8 GPa.

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Grain boundary phase transitions

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Grain boundary (GB) phase transitions can change drastically the properties of polycrystals. 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 numerous systems 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. The experimental data on GB segregation, energy, mobility and diffusivity obtained in various systems both in polycrystals and bicrystals are analysed. In case if two solid phase are in equilibrium, the GB "solid state wetting" can occur. In this cas the layer of the solid phase *2* has to substitute GBs in the solid phase *1*. Such GB phase trasition occurs if the energy of two interphase boundaries is lower than the GB energy in the phase *1*.

Faceting is a well documented phenomenon known both for surfaces and interfaces, particularly, grain boundaries (GBs). 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 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). In most cases the GB facets lie in the CSL planes with high density of coincidence sites. Phaseting and roughening GB phase transitions are analysed for the twin GBS in case of exact CSL in Cu and strained CSL in Zn.

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Role of interfaces in polymorphic phase changes in nanocrystalline early transition metals

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High-energy mechanical milling of elemental powder leads to significant grain refinement through a process of welding, fragmentation and dynamic recrystallization. We have earlier reported that elemental niobium undergoes a metastable bcc $\rightarrow$ fcc polymorphic transition in planetary ball milling [1]. Recently, we have detected a similar polymorphic change in elemental titanium and zirconium (hcp to fcc) induced by high-energy mechanical milling [2-3]. The transformation remains incomplete unless the total strain and strain rate are adequate. Careful estimation of substitutional/interstitial impurity levels and resistivity measurements rules out the possibility of the milling products being single-phase nitride/carbide/oxide like ceramic phases. Experimental evidences in terms of x-ray diffraction and high-resolution transmission electron microscopy show that the transformation is gradual and complete only below a minimum grain size level. Thus, it is believed that nanocrystallization is a prerequisite for structural instability that propels this change in crystal structure. The structural instability seems to arise due to the large negative hydrostatic pressure acting at the increased area fraction of interfaces and related strain energy accumulation following nanocrystallization below a critical grain size. The transformation seems irreversible in nature. In the present paper, we will utilize our earlier model [1] to explain the genesis of polymorphic changes in these three early transition metals (Nb, Ti, Zr) by mechanical milling.

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Triple junction motion and grain microstructure evolution

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Classical views of grain growth in polycrystals are based on the concept of dominant and exclusive role of grain boundaries in this process. It is reflected in well known Von Neumann-Mullins relation. According to this approach triple junctions do not disturb grain boundary motion and their role in grain growth is reduced to preserve the thermodynamically prescribed equilibrium angles at the lines where boundaries meet.

However, several recent theoretical and experimental studies provide evidence that the kinetics of triple junctions may be different from the kinetics of the adjoining grain boundaries. This affects the kinetics of microstructure evolution during grain growth.

In the present work the experimental data of triple junction mobility are considered. Then the the process of grain growth in 2D systems is analysed with respect to the controlling kinetics: from solely boundary kinetics, when grain growth in a polycrystal is determined by the Von Neumann-Mullins relation, to exclusively triple junction kinetics, when grain growth is governed by the mobility of triple junctions. It is particularly emphasized that the angles in the tip of triple junction and the behaviour of grain boundary system with triple junctions are completely defined by the dimensionless parameter Λ, which, in turn, is a function of not only the ratio of triple junction and grain boundary mobility, but of the grain size as well. Thus, the term „triple junction of low mobility“ is equivalent to a „small value of Λ “.

It is shown that in the "intermediate" case, when the driving force for grain boundary motion and the characteristic mobility are grain boundary curvature and grain boundary mobility, respectively, a limited mobility of triple junctions essentially influences grain boundary motion. The Von Neumann-Mullins relation does not hold anymore, and this is the more pronounced the smaller the triple junction mobility. What’s more dragging effect of triple junctions changes qualitatively the structure of the Von Neumann-Mullins relation. For the finite mobility of grain boundary triple junctions this relation is split into 2 branches – for growing and shrinking grains respectively. The grains which are situated between these branches remain invariant, what increases drastically the stability of fine grained materials in the course of grain growth. The theoretical consideration is exemplified by computer simulation study of grain growth in 2D systems.

Coherent γ′-precipitates at singular and rough grain boundaries in model Ni-base superalloys

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In model Ni-base superalloys, the singular and rough grain boundaries which exist at a temperature range between 1050 and 1200ºC can be identified by observing the shapes of coherent γ′-precipitates by transmission and scanning electron microscopy. Some grain boundaries become locally curved with the impinging γ′-precipitates. These grain boundaries must be rough. Some grain boundaries maintain their flat shapes even at the contact areas with the γ′-precipitates and triple junctions. Such flat grain boundary shapes indicate that these grain boundaries are singular. Some grain boundaries have hill-and-valley shapes and some of their segments also show flat shapes with impinging precipitates. These boundary segments must also be singular. The results confirm that both singular and rough grain boundaries exist in this alloy at this temperature range. The interface between γ-matrix and coherent γ'-precipitates appears to be rough, and the precipitates thus show dendritic growth.

Thermodynamic approach for the grain boundary diffusion compensation effect

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The paper is devoted to the problem of the compensation effect for grain boundary (GB) diffusion, i.e. the linear dependence of the logarithm of the pre-exponential factor of the GB diffusion coefficient on the activation energy. The experimental data on GB diffusion of Zn in Al bicrystals [1, 2] are presented in terms of the activation entropy and the activation enthalpy. It is proposed to attribute the compensation effect to a first order phase transition from the ground state to the activated state during thermal activation. It is shown that the thermodynamic properties of the activated state, or a barrier phase, are closed to the properties of Al-Zn eutectic. This circumstance allows us to perform the thermodynamic analysis of the co-existence of ground state and the barrier phase on the basis of Clayperon-Clausius equation. The data on GB diffusion of Zn in Al bicrystals under high pressure [3] are involved to establish the dependence of the compensation temperature, T_c, on pressure. It is shown the activation energy and the activation volume for GB diffusion are co-related parameters and the ratio of these two parameters is, in fact, a constant. This experimental fact confirms the validity of our approach to describe the compensation effect for GB diffusion as a first order phase transition between the ground state and the barrier phase. The numerical relationship $T_c = f(p)$ is derived.

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Faceting of Σ3 and Σ9 grain boundaries in Cu

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Faceting is a well documented phenomenon known both for surfaces and interfaces, particularly, grain boundaries (GBs). 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 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). In most cases the GB facets lie in the CSL planes with high density of coincidence sites. For the investigation of GB faceting a cylindric Cu bicrystal with an island grain was grown with the aid of the Bridgman technique from Cu of 99.999 wt.% purity. Grain *1* in this bicrystal is completely surrounded by grain *2* forming the Σ9 <110>tilt GB. The <110> axes in both grains are parallel to the growth axis. The faceting was analyzed in an *as-grown* bicrystal and after annealing at 1020, 800, 700, 600 and 400°C. It is well documented in the literature that close to the {111}/{115} inclination the Σ9 GB is unstable against the dissociation reaction: $\Sigma 9 \rightarrow \Sigma 3 + \Sigma 3$. This dissociation proceeds also in our case. The twins appear during the growth of the bicrystal instead of $\{111\}_1/\{115\}_2$ or $(110)_{\Sigma 9CSL}$ facet. The profiles of the the formed GB thermal groove were analysed with the aid of atomic force microscopy. Wulff-Herring plots and GB phase diagrams have been constructed for the Σ3, Σ9 and Σ9+Σ3 GBs. The energy of the symmetric Σ3 twin ($\{111\}_1/\{111\}_2$ or $(100)_{\Sigma 3CSL}$ facet) is very low in case of exact coincidence. The second close packed plane ($\{211\}_1/\{211\}_2$ or $(010)_{\Sigma 3CSL}$ facet) is the so-called asymmetric twin. The $\{211\}_1/\{211\}_2$ facets are well documented for Al, Au, $AuCu_3$ and Ge. However, the twin plates in Cu and Ag are not rectangular. The end facet form an angle of 82° with the $\{111\}_1/\{111\}_2$ or $(100)_{\Sigma 3CSL}$ sides. Previous studies 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. However, the analysis of the literature shows that the 82° facet appears only at high temperatures. At low temperatures the "normal" 90° $(010)_{\Sigma 3CSL}$ facets are present also in Cu. Below 800°C less densely packed CSL facets gradually appear in our samples. Therefore, the numerous GB faceting phase transitions occur between 0.95 and 0.4 of the absolute melting temperature.

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Grain boundary wetting of polycrystalline Ni by liquid Pb: influence of grain boundary misorientation and plane position

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Grain boundary wetting by liquid metals is a complex phenomenon that is of great technological importance in liquid metal heat exchangers, sintering and soldering. The mechanisms of this phenomenon are not yet well understood. The goal of this study is to investigate the influence of GBs character on their wetting.

Solid Ni / liquid Pb system was chosen because these metals do not form any intermetallic compound and Ni has a limited solubility in liquid Pb at the experimental temperature(740° C). An experiment consists in depositing a Pb droplet pre-saturated in Ni on a high purity large-grain Ni substrate in pure He at 740° C, holding at this temperature for a given time and cooling at room temperature. Several techniques were used for *post mortem* investigation of former solid-liquid interfaces: (i) the sample was cut perpendicularly to the interface and characterised by SEM to determine the shape and the linear dimensions of intergranular films, (ii) the solidified lead droplet was selectively dissolved in a H_2O_2-CH_3COOH mixture in order to examine the solid-liquid interface by optical microscopy and SEM, (iii) ~0.5×0.5×10 mm bar including a part of solid-liquid interface was machined from Pb-Ni sample and investigated at ESRF Grenoble with high-resolution X-ray microtomography (this technique allows to reveal lead distribution inside Ni polycrystal), (iv) finally EBSD was used to find out the misorientation of Ni grain boundaries and relate wettability of GBs with their geometry.

It was found that GBs of Ni could be devided into three groups: (i) wetted by lead with formation of long (up to 200 μm) and thin (about 1 μm) channels with several facets in the vicinity of channel root, (ii) attacked by lead with formation of V-like micron-size grooves, (iii) not attacked by lead (at least after several hours). There is a direct relation between type of GB (according to CSL formalism) and its wettability by liquid lead: all high-angle general GBs were wetted while special GBs were either wetted, grooved or not attacked depending on Σ value. A strong effect of GB plane position on wettability was revealed. It was illustrated by a difference in wettability of coherent and non-coherent GBs formed between the same grains. Fast (as compared to GB wetting) penetration of liquid lead along triple junctions was observed.

Analysis of grain boundary segregation in Cu-Sb alloys

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The results of the study of Sb grain boundary equilibrium segregation in Cu-based alloys by AES and XPES methods are analysed. The Sb concentration changed from 0,33 to 2,56 at.% at temperature range from 673 to 1073 K. By the use of Langmuir-McLean isotherme the Sb saturated concentration was calculated, e.g. at the filling of all available cites at the first layer in equilibrium with other layers and the bulk. The values of do not exceed Sb concentration in chemical compounds in equilibrium with solid solution. The obtained value of grain boundaries segregation capacity for Sb in Cu-based alloys is in the range between 0,38 and 0,65 monolayer.

Enthalpy and entropy of segregation are equal to 8,9 kJ/mol and 6,2 kJ/mol consequently.

Correlation between structure, segregation and electrical activity in Ge(S) grain boundaries

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In the present study, structural modifications induced by equilibrium sulfur segregation in pure tilt germanium {710} <001> Σ=25 (θ=16.26°) and {551} <011> Σ=51 (θ= 16.10°) grain-boundaries (GB) were investigated using high-resolution electron microscopy (HREM) coupled to electron energy-loss spectroscopy (EELS). This experimental approach was supported by structural modeling and image simulations. Our results showed that the as-grown ∑=25 GB is composed of two parts: a stable structural region and a variable perturbed core. On the basis of our simulations, no unique model fits with the experiment and thus we concluded that this GB can only be formed by a multiplicity of configurations. After the sulfur segregation treatment, sulfur enrichment in the GB was revealed using Energy-filtered transmission electron microscopy (EFTEM). As a result, drastic changes in the structure of the GB were observed [1].

To take this analysis further, a simpler GB structure, that is germanium ∑=51, was studied. The structure of such a GB is made of a well known configuration, namely a Lomer-dislocation, which is basically a five-fold ring adjacent to a seven-fold one. After sulfur treatment, HREM imaging also showed significant contrast modifications apparently concentrated on the dislocation core. Chemical imaging again indicated the presence of sulfur enrichment along the GB plane, strongly reinforcing the idea that equilibrium sulfur segregation in the germanium (sulfur) system occurs into the GB. This confirms our previous results obtained on Σ =25 GB. One can therefore argue that it is the presence of those odd-numbered rings in the GB, which own a specific crystallographic and electronic nature, coupled to the electronic properties of sulfur that are responsible for the preferential segregation into the GB. Electrical measurements [2] were also carried out on both bicrystals before and after sulfur segregation. Prior to segregation, preliminary results clearly show the existence of electrical recombination sites of minor carriers located at the GB. After sulfur segregation, the GB electrical activity disappears and the bicrystal behaved electrically as single crystal. In order to correlate the recombination centers to the segregation atomic sites, investigation of different Ge bicrystals is underway.

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Grain boundary structure and properties of bulk spd nanostructured materials

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Severe plastic deformation (SPD), i.e. intense plastic straining under high pressure, is an innovative technique for producing bulk ultrafine-grained nanostructured metals and alloys. SPD-produced nanostructures can lead to extraordinary properties which, however, depend strongly on the microstructure feature, especially grain boundaries structure-misorientation parameters, types and density of grain boundary defects. The present paper focuses on examples of SPD-processed metallic nanomaterials with such unique functional and mechanical properties as very high strength and ductility, superplasticity and shape memory effect. The grain boundary structure-new properties relationship in SPD-produced materials is considered and discussed on the basis of thorough TEM/HREM and X-ray investigations of these materials.

Features of grain boundaries in melt-quenched crystals

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In this report we will have tried to present the information concerning the grain boundary structures formed directly during the melt quenching. We have considered the structure of binary and ternary melt quenched Fe-based alloys. After melt quenching the crystallite (grain) size is varied from several tenth of micron up to several microns. Grains are equiaxed or elongated in the normal direction to the ribbon plane depending on the ribbon thickness. The main peculiarities of the grain structure are:

The existence of the well developed subgrain structure with different degree of perfection.

Nonequilibrium character of the grain boundary structure which is evidenced by the well developed surface of grain boundaries and frequent variation of the grain boundary plane orientation. Besides, this is also evidenced by the high density of defects (dislocations and submicroporosity) in the boundary plane.

High thermal stability of the grain structure. As was shown experimentally, the noticeable grain growth occurs at the temperatures of 800-900^{o}C depending on the alloy composition. Dislocation prismatic loops and vacancy clusters show the clear tendency to segregate at the grain boundaries and cell boundaries. The dislocation loop segregation inhibit the grain boundaries migration very much and may be the reason of the above mentioned high thermal stability of grain structure.

Sharp (on the order of magnitude) selective grain growth occurs at temperatures higher than 1000^{o}C in the Fe-Si alloys. This process is accompanied by the sharpening of the crystallographic texture relative to the weak texture of the as-quenched state. The texture component {110} in the ribbon plane is most enhancing. Certainly, this phenomenon resembles the secondary recrystallization process in the cold worked crystals. Hence, we named this process as the quasi-secondary recrystallization in the melt quenched alloys.

Melt quenching includes the stage of the rapid crystallization. because of these grains have well developed internal cell substructure. Experiments have shown that in the most cases solidification proceeds by the motion of the cellular crystallization front caused by the existence of the zone of concentration undercooling of the melt. As a result, dendritic cells are formed in the interior of the grains with the size smaller than a grain size. Cell boundaries and grain boundaries are forming two subsystems with different scales. The diffusion dissolution of the dendritic cells and complete chemical homogenisation occur under the thermal influence (at 600-700^{o}C).

Low energy plasma immersion ion implantation of 52100 ball bearing and 304L austenitic stainless steel

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Plasma immersion ion implantation (PIII) is an advanced plasma-assisted surface engineering technique to enhance resistance to wear, corrosion, etc. PIII of nitrogen was carried out in pulses of 3.8 kHz frequency to modify the surface of AISI 52100 ball bearing and 304L stainless steel at high dose but low negatively biased (–1 to –10 kV) d.c. potential and an elevated temperature of 300 – 500^{o}C for 1-5 h. PIII seems to significantly enhance the hardness (up to 1200 VHN) confined to a shallow depth from the surface (up to about 40 μm). However, PIII appears to adversely affect the resistance to pitting corrosion of stainless steel. A detailed characterization of the surface microstructure, composition and chemical-state of the constituents was carried out by normal and glancing angle X-ray diffraction (GAXRD) and by X-ray photoelectron spectroscopy (XPS), respectively. The microstructure of the plasma ion implanted zone mostly consists of ferrite and Fe-nitrides in ball bearing steel, and alloyed austenite (γ), expanded austenite (γ_N) and ε-nitride in stainless steel, respectively. A simple kinetic analysis reveals that nitrogen diffusivity in PIII is an order of magnitude faster than the relevant diffusion rate of nitrogen in plain carbon or low alloy steel. In general, increase in hardness could arise due to grain refinement and/or solid solution hardening. On the other hand, deterioration of corrosion resistance could be attributed to the evolution of a multiphase microstructure (γ, γ_N and particularly ε_N) from an essentially single-phase matrix. Finally, a detailed analysis is presented to identify the optimum PIII condition that offers the desired property at the surface of either grade of steel.

Electromigration in microelectronic interconnects: coupling electrotransport in small dimension to interface reactions

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Electromigration (EM) in thin film interconnects is basically the interface diffusion electrotransport problem; important however is that the EM rate is not necessary electrotransport controlled. In advanced interconnects, which are either short or separated into short polygranular segments, it can be controlled by the rate of atomic detachment /attachment processes ("interface reactions") which act in series with electrotransport. To reduce EM failures, the microscopic mechanisms of these reactions must be understood and their kinetics coupled to that for electrotransport.

In this lecture we review the topic from the perspective of our own contribution to the field, present the result of analytical and computer modeling, and compare them with drift velocity EM kinetic data for Cu and Al interconnects. This enables to describe the mechanisms of the anode and cathode reactions, their effect on the total rate of EM, and understand how alloying elements can affect the EM rate through their influence on the reaction rates.

Covered are the following issues:

1. Interface electrotransport: which are the major interfaces involved?
2. Interface grooving as the cathode reaction: grooves as the carriers of EM displacement.
3. Stress relaxation by GB diffusion creep as the anode reaction: creep controlled EM regime in short lines
4. Segregation effects in electrotransport, grooving, and creep in miniaturized interconnects.
5. Transition to reaction controlled regime: characteristic feature of all migration processes under potential fields (stress-, thermo- …) in small dimension microelectronic conductors

A new approach to grain boundary engineering for structural and functional materials in the 21st century

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In the last decade, the importance and the usefulness of grain boundary engineering in advanced materials were increasingly recognized since the time when the concept of grain boundary design and control was proposed by the author early 1980's [1]. The early stage of basic research of grain boundary design and control was involved mainly in structural materials, aiming at the control of the brittleness associated with intergranular fracture caused intrinsically or extrinsically, which was the most important problem in structural materials [2]. More recently grain boundary engineering has been extended to functional advanced materials [3]. Moreover, the grain boundary becomes increasingly more important with decreasing the grain size in polycrystalline materials, particularly nanocrystalline materials.

The preset paper is an overview of recent work of grain boundary engineering in structural and functional advanced materials, including metallic, semiconductor and ceramic materials. In particular, a new approach to grain boundary engineering has been attempted by using the application of external fields, such as magnetic field, ultrasonic wave and large temperature gradient associated with rapid solidification from the melt. It is emphasized that the control of the grain boundary character distribution (GBCD) and the grain boundary connectivity are important factors controlling grain boundaries to obtain desirable bulk properties in polycrystalline advanced materials, particularly in nanocrystalline materials. A new understanding of the Hall-Petch type relationship is given for the grain size dependence of bulk properties, such as the fracture stress. Grain boundary engineering in polysilicon has been performed to develop a high performance solar cell, and obtained knowledge is introduced although it is still on the half way.

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Phase formation in diffusion-soldered Cu/In-Sn/Cu interconnections

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Lead-free interconnection technology becomes growing interest mainly because of a strong concern to protect the environment particularly due to harmful effect of lead and the use of toxic fluxes like chlorofluorocarbon for conventional soldering. Therefore, new solder materials are searched which could replace the commonly used lead-tin solders, especially in electronics production. For example, heat dissipating power components such as chip resistors cannot be connected to leads using a conventional soldering process. This results from the main limitation of the soft soldered joints like working temperature, which is 60-100 °C below the soldering temperature (typically 220-260 °C for Pb-Sn solders).

One of the promising techniques, which has a large potential to be applied for the formation of thermally and mechanically stable bonds up to 400-600 ^{o}C, is based on the principle of isothermal solidification in a technological process called diffusion soldering [1-3]. A metal of low melting temperature is sandwiched between the substrates of relatively high melting temperature. During heating of such assembly at a temperature above the melting point of the low melting component the joint is formed, entirely consisting of intermetallic phases having melting temperatures much higher than the temperature used for the fabrication of the joint.

The present paper reports the recent experiment performed in order to obtain diffusion-soldered Si/Si interconnection using eutectic In-Sn alloy (48 at.% In) as filler material and Cu as interlayers. The eutectic In-Sn alloy, because of its low melting temperature (120 °C**),** offers advantage over other filler materials like Sn, In or Ag. The material was prepared according to procedure described in detail in Ref. [4]. Application of transmission electron microscopy with an attachment for high resolution chemical analysis allowed to characterize the crystallographic, microstructural and microchemical details of the processes occurring during joint formation at 200 °C. The η phase based on Cu_6Sn_5 existed in the central part of the joint. With increasing distance from the middle of the joint, amount of In also increases replacing Sn and promoting formation of the η phase based Cu_2In. The phase adjacent to Cu_2In was identified as ξ ($Cu_{10}Sn_3$) phase of the following composition Cu=74.1÷77.2, Sn=14.5÷14.7, In=8.3÷10.2 (at.%). In the narrow region adjacent to the Cu substrate the next phase also appeared. This phase could be described as modified δ phase (Cu_7In_3) with a=1.007 nm, b=0.9126 nm and c=0.6724 nm, α=90.22^{o}, β=82.84^{o}, γ=106.8^{o}) with the following composition: Cu=68.9÷72.3, Sn=9.1÷10.8, In=16.9÷22 (at.%).

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Mass transfer in multilayered thin-film Cr/Cu/Ni sistem under laser-pulse heating

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The laser – induced mass transfer in thin – film Cr/Cu/Ni system has been studied by means of Auger Electron Spectroscopy. For the laser – pulse energy values of E=100-170 mJ the diffusion of Cu atoms into, and their accumulation within the Ni layer are observed, whereas at E>170 mJ the same is true for Cr atoms. The observed phenomena are explained on the basis of calculation temperature distribution in the system during the laser action. Enhanced transfer of Cr atoms towards external surface is observed under the irradiation regimes leading to the melting of intermediate copper layer. Diffusion coefficients of copper and chromium calculated from their surface accumulation show an exponential dependence on the laser – pulse energy. Under the laser heating the diffusion processes are more pronounced as compared to those under conventional thermal annealing. This is accounted for higher concentration of nonequilibrium defects generated within the irradiation.

The interface design of thin film system based on solid state electrolyte ($RbAg_4I_5$) as a way towards supercapacitors

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Supercapacitors are energy storage devices with a very high capacitance and a low internal resistance. The operating principle of the supercapacitor is based on an electric double layer appearing at the electrolyte–electrode interface. The aim is to gain control of materials and devices at the atomic level, allowing us to design materials with properties tailored needs of High.Tech. Nature's achievements are therefore benchmarks for our increasing control of materials and their properties. In this work we used modern knowledge of interface atomic structure and properties and try on this base to mimic and optimized microdevice functions such as capacitance of some double layer thin film structures. The isomorphous solid electrolyte–superionic conductors of the $RbAg_4I_5$ family with record Ag+ conductivity at RT~0.3$\Omega^{-1}cm^{-1}$ and concentration of Ag+ ions >10^{22} cm^{-3}, especially the $CsAg_4Br_{3-x}I_{2+x}$ (x~0.3) solid electrolytes, synthesized for the first time in IMT RAS [1-2], were used for fabrication of many heterostructures (thin film supercapacitors). The advantage of the $CsAg_4Br_{3-x}I_{2+x}$ is its stabiliy in the contact with metallic silver (the reverse electrode relative to Ag+ ions). We used for comparative interface analysis also the data of the patents [3-4], in which for the first time non-polarity capacitors with n+ Si working electrodes were created.

The capacitance of electric double layer supercapacitor can be very large, thanks to the very small distance which separates the opposite charges at the electrolyte-electrode interfaces, very huge surface of the electrodes and high dielectric constant of electrolyte. In this paper we analyze all these modifying factors on the base of interface coherency, interface atomic width and charge. New types of chemically inert electrodes are proposed, some new interface phenomena (as sharply increasing of the capacitance at room temperatures when the relative humidity of air rises within the limits 0-50%) are explained due to interface crystallochemical analysis and computer modeling.

Thin film solid state electrolytes are good candidates for their use in Microelectromechanical Systems (MEMS) especially in new trend in MEMS industry called "system on a chip".

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Stacking-fault-type interfaces ascertained by γ-surfaces: Their role in plastic deformation of elemental solids and compounds

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The stacking-fault-like planar defects, formed by joining two parts of a crystal that have been relatively displaced with respect to each other, are interfaces which play a crucial role in crystal plasticity. When they are metastable, dislocations may dissociate into partials connected by such faults and this is the most important factor that determines operative slip systems in a given material.

In this presentation, we employ the concept of energy-vs-displacement surfaces, called γ-surfaces [1, 2]. Minima at such surfaces determine metastable interfaces of the stacking-fault type. For each specific crystal structure, it is in the first place its symmetry that governs the most general features of γ -surfaces. These features are then common to all materials crystallizing in this structure. On the other hand, differences found for different materials with the same crystal structure are controlled by the specific character of interatomic bonding. Both these aspects of γ -surfaces and metastable stacking-fault-like planar defects will be first briefly discussed for elemental solids. This will be followed by the analysis of such faults in various types of intermetallic compounds. In particular, we shall concentrate on those compounds the mechanical behavior of which has been studied extensively because of their possible applications as high-temperature materials. These are cubic $L1_2$ alloys, such as Ni_3Al, tetragonal alloys of $L1_0$ and $D0_{22}$ type, specifically TiAl and Al_3Ti, hexagonal DO_{19}, such as Ti_3Al, and tetragonal C11b, represented by $MoSi_2$ [3]. Ultimately, we shall discuss the role these interfaces play in the plastic deformation of these compounds and how their structure and energy affects ductility of these materials.

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Ab-initio modelling of particle diffusion and adhesion of metal overlayers on oxide surfaces

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Though oxides are widespread, the knowledge of their surface properties and their interfaces with other species, such as atoms, molecules, and insulating or metal overlayers is still rather involved. This is mainly due to the extreme sensitivity of the oxide stoichiometry to the actual thermodynamic conditions, which can alter the O content and deeply modify the atomic-scale surface morphology and reactivity. The study of their behavior in variable external conditions thus needs great care in preparing and conducting the experimental measurements. Presently, the existing gap between the ideal laboratory conditions (controlled partial pressures and temperatures) and those existing in the real world (geologic conditions, heterogeneous catalysis, industrial processing) is very far from being filled.

On oxide surfaces, the spatial variations of the intense electrostatic potential and the occurrence of defects (O vacancies, ad-atoms, steps, etc.) are generally accompanied by a modification of the charge state of the atoms, which gives rise to a strong interplay between atomic and electronic structures, with important consequences on adhesion, diffusion, and reactivity [1]. First-principles simulations are particularly useful in this framework, since very few ad-hoc hypothesis are made on the nature of the chemical bonding, which makes them suitable to understand the fundamental processes at the atomic scale.

In this talk, we will take MgO as an example to illustrate the capabilities of ab-initio methods on few selected problems. Firstly, we discuss the (2x2) reconstructions of the polar MgO(111) orientation. Only the combination of first-principle simulations with grazing x-ray diffraction experiments permits to propose a reliable structural model, which includes the presence of Mg overlayers onto an O-terminated ideal MgO(111) surface. Then, we discuss the electronic properties of other metals deposited on the same surface, stressing the role played in curing the polarity.

In the second part of the talk, we show the adsorption and diffusion of some atomic and molecular species involving Mg and O on the cleavage MgO(100) surface [2]. This study constitutes an essential premise to build larger scale models for the homo-epitaxy of MgO, taking into account the relevant reactions at the surface.

In all cases, the ab-initio results are complemented by simpler models that help to generalize the numerical outcomes to other systems.

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Mesoscale and atomic modeling of junction disclinations due to finite length of grain boundaries

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At IIB'92 Alex King [1] demonstrated that junction lines of short grain boundaries can contain disclinations, which are caused by a discrete nature of the dislocation structure of boundaries. These disclinations arise when the length of a boundary is not an integer multiple of the period of the grain boundary dislocation network and compensate a difference between the actual misorientation angle of the finite boundary and the misorientation required to fulfill the junction condition. In the present paper the origin of these compensating disclinations within triple junctions is elucidated and their strength is calculated using the disclination-structural unit model [2]. It is shown that for a GB with length of about 10 nm the junction disclinations can have a strength value of about 1°. Elastic energies of triple junctions due to compensating disclinations are calculated for both equilibrium and non-equilibrium structures of a finite length GB, which differ by the position of the grain boundary dislocation network with respect to the junctions. The calculations show that triple junction energies are comparable to dislocation energies. Therefore, for very small grain sizes compensating disclinations induce elastic fields corresponding to a very high effective dislocation density $\rho = d^{-2}$ and can play a significant role in the properties of nanocrystalline metals.

Atomic structure of a triple junction of [001] tilt boundaries Σ=5/53.13°+ Σ=5/53.13°+Σ=25/73.74° in Ni is simulated using embedded atom method. Varying the position of the Σ=25/73.74° boundary structural units with respect to the junction and thus varying the disclination content of the junction the junction energies are calculated and compared to the predictions of the disclination-structural unit model.

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Theory of non-equilibrium grain boundaries and its applications for nano- and microcrystalline materials processed by ecap

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Basic principles and methods of non-equilibrium grain boundary theory are presented. Concepts according to which the non-equilibrium grain boundary state depends on the grain boundary free volume changes caused by their interaction with lattice defects, in particular with dislocations, are in the basis of the theory.

Non-equilibrium states of the grain boundaries in nano- and microcrystalline metals processed by equal channel angular pressing (NMC-ECAP metals) were analyzed. It was shown, that non-equilibrium GB state in such materials may be provided by initial non-equilibrium state, as well as by non-equilibrium state caused by embedding dislocations into the boundary during GB migration and/or materials deformation.

Examples of the presented approach use for describing NMC-ECAP materials behavior were analyzed. Abnormal grain growth, internal friction characteristic features and strain hardening in case of high strain rate superplasticity brief description were presented.

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Microstructure and grain boundary statistics in ultrafine-grained nickel

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Considerable interest has developed recently in processing bulk materials through the application of severe plastic deformation (SPD). These procedures are attractive because, unlike alternative processes involving nanopowder compaction or gas condensation, they are capable of producing large bulk samples free of any residual porosity. Two methods of severe plastic deformation for grain refining and their combination were employed to fabricate ultrafine-grained samples of pure nickel. The microstructures with a mean grain size of about 350 nm for nickel samples by equal channel angular pressing, 170 nm for samples by high-pressure torsion and about 100 nm by their combination were attained. All samples were characterized using microhardness measurements, x-ray difractometer, transmission electron microscopy and orientation imaging microscopy. Thorough investigation of texture, microstructure and grain boundary misorientation distribution for all samples has been carried out. It was accomplished that combination of ECAP and HPT leads to a deeper refinement of nickel samples possessing homogeneous and equiaxed microstructures.

Grain boundary diffusion and ductility of polycrystalline and nanostructured materials

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The main role of the diffusion-controlled processes at the grain boundaries on the development of plastic deformation during high temperature creep and superplasticity is discussed. It was found that the activation of grain boundaries by the action of impurity grain boundary diffusion fluxes from environment (coating) leads to the acceleration of grain boundary sliding and realization of short-time superplastic state in coarse-grained polycrystals.

By way of example of nanostructured nickel and copper, processed by severe plastic deformation, it was established that the temperature which corresponds to the maximum of the effect of creep resistance decrease under the action of grain boundary diffusion fluxes is by several hundreds degrees low in case of nanostructured metals in comparison with the corresponding one for coarse-grained metals.

New experimental data on the investigation of the physical nature of high-rate and/or low-temperature superplasticity of nanostructured Al-Mg-Li allows are represented.

Structure of microcrystalline superplastic aluminum based alloy

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Structure of Al based alloy (Al – 5.5% Mg – 2.2%Li – 0.12%Zr) processed by equal channel angle (ECA) pressing was investigated. The obtained material was mechanically tested by uniaxial tension with a constant deformation rate from 0.5 to 50 mm/min. Deformation temperature was 370°C. During the tests the alloy specimens demonstrated superplastic flow. The maxim elongation was about 1900%. Structure and phase composition of the specimens were investigated by TEM and X-ray diffraction analysis. We used $g \cdot b$ and trace analysis to characterize subgrain structure of the alloy.

It was shown that the mean grain size in ECA pressed material was about 1.6 μm. Grains were equiaxial with a developed substructure. There were individual dislocations, piles-up and also rather regular subboundaries in the grains.

Plastic deformation of the specimens resulted in some structural changes. Dislocation density into the grains decreased, shape of the grains became elongated, their mean size increased.

Dislocation structure of the subboundaies was investigated in details. The plane of subboundaries, Burgers vectors and type of the dislocations in them were determined both in the initial material and after superplastic deformation. It was shown that the subboundaries were sufficiently non-equilibrium because of a mixed character of the dislocation formed the subboundaries and because their planes do not coincide with those for equilibrium ones.

Conventional, weak beam and in situ TEM studies of dislocation reactions at grain boundaries

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Dislocation reactions at interfaces play an important role in the first plastic deformation stage of polycrsytals. Models have been proposed to explain stress accommodation in the neighbouring crystals or within the grain boundaries [1,2] and detailed processes have been simulated for some particular interfaces [3]. But, relatively few experiments have been performed on different types of grain boundaries and on different materials. The purpose of this work is to present and to compare dislocation interactions with interfaces in two metals: nickel [4,5] and copper displaying a high and a low stacking fault energy, respectively. The experimental results are also compared to the simulated ones when available.

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Thermodynamics of curved interphase boundaries in nanosystems

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Now the thermodynamics of flat interphase boundaries ($r = \infty$) is full enough advanced within the framework of final depth layer method (the method of Van-der-Vaals-Huhhengeim-Rusanov) and sectioning surface of Gibbs [1]. Many authors in different time offer the theories permitting to find relations of interface tension σ and concentrations of components $x_i^{(\sigma)}$ on such boundaries from basic parameters of system state [2]. In turn knowledge σ and $x_i^{(\sigma)}$ at the boundary of two condensed phases (α,β) and also these condensed phases at the boundary with saturated (γ) vapours ($\sigma^{(\alpha\gamma)}, \sigma^{(\beta\gamma)}$) allow to find the characteristics of three-phase equilibrium. The very handy for practice use relations obtain at usage of rigid system model being a quite good approaching in application to surfaces of condensed phases [1,3].

In the present paper the new results of the authors on the thermodynamics of curved interphase boundaries ($r \neq \infty$) encompassing area of nanosizes are set up. The new equations of interface tension isotherms and structures of interphase layer and coexisting phases in the integral form are adduced. They are obtained, outgoing from the general conditions of phase equilibrium in a system within the framework of a thermodynamic final depth layer method. In particular cases from the obtained expressions follow known Ostvald-Froindleht formula for dissolubility of small-sized crystals, decreasing melting temperature of crystals depending on degree of dispersion, change of surface tension with change of radius of curvature in an one-component system (the equation of Tolmen) and other. At transition to flat boundaries the new integral relations pass in the conforming expressions obtained earlier by one of the author [3]. The method of finding the work of adhesion W, wetting contact angle θ and spreading coefficient K_s in systems with curved boundaries is set up depending on the size of a liquid phase. The qualitative criterions of limiting interphase activity of components (σ, W, θ, K_s) in systems with curved boundaries at the small components of dopes are discussed ($x_i \to 0$).

In the paper the results of concerted calculations of interface tension, the structure of a transient layer, the work of adhesion, the wetting contact angle and the spreading coefficient of nanometers drops on a surface of solid solutions in metallic systems depending on radius of curvature, temperature and structures of bulk phases (In-Pb, In-Sn) are adduced.

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The interface design and magnetic properties of sintered permanent magnets of $SmCo_5$ – type

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The sintered permanent magnets (SPM) based on powders of rare earth metals are nonequilibrium multiphase systems. The processes of structure selforganization giving rise to special crystallographic and magnetic textures are characteristic of these systems. The excellent magnetic properties of SPM can be obtained by improving strong requirements on the grain and interface structure.

The influence of interface structure, boundary secondary phase distribution and chemical composition on the magnetic properties of SPM based on $SmCo_5$ high dispersion powder is investigated. The phenomenon of high coercivity of $SmCo_5$ magnets has been treated in the framework of the theory of interfaces (calculations of the crystallographic parameters and atomic models of special coherent grain and phase boundaries in the Sm-Co- system), which affords some new insight in its origin.

The crystallographic parameters and boundary structure models for the Sm-Co system are determined. A calculation model is proposed for phase distribution corrected for the real oxygen content and magnet density.

The texture analysis and precipitation processes of secondary phases on grain boundaries are compared with interface crystallography. It found that the coercivity of $SmCo_5$–powder based magnets is strongly influenced by the perfection of intercrystalline boundary structures and secondary phase and pore distribution in the microstructure.

High coercivity magnets have predominant {111}R={0001}H texture, which facilitates the formation of the spectrum of low–energy special twist tilt boundaries with mutual grain rotation axis, coinciding with the earthy magnetization axis. Such boundaries posses a perfect structure and are almost defect-free, that determine high magnet density and prevent reverse magnetization domains formation.

Proton conductivity in composite systems containing inorganic hydrates

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Proton conductivity, cation sorption and surface morphology were studied for heterogeneous composite systems containing hydrated zirconia, hydrated zirconium and tantalum acid phosphates. Inorganic hydrates were modified using chemical interaction on the surface and physical mixing. All obtained materials were investigated with the help of impedance spectroscopy, potentiometric titration, thermogravimetric analysis, electron microscopy and X-ray probe spectral analysis.

It was shown that charge transfer in pressed powder of hydrated zirconia occurred in a thin layer of pseudoliquid phase, which was formed on the particle surface. Conductivity of the initial substance decreased significantly at low humidity or at high temperatures due to dehydration processes (from $2*10^{-5}$ at 20°C to $1*10^{-7}$ S/cm at 400°C). However after heating at 300°C with further exposure on air at room temperature they became much more conductive ($1.2*10^{-4}$ S/cm). Conductivity values significantly increased (up to $2.7*10^{-4}$ S/cm) after additional cycle of heating. The water content of the obtained oxides did not exceed 40% from that of the initial particle hydrate. The ion exchange rate increased significantly for the hydrated zirconia, which had been preliminary heated. Moreover ion-exchange capacity of these compounds slightly increased after heating. The investigation of the hydrated zirconium oxide by means of electron microscopy and X-ray spectral microanalysis showed that heating and following surface rehydration of zirconia caused particle size decrease, surface area increase and migration of defect centers to the near-surface layer. Such surface reorganization allowed us to enhance transport and sorption properties of the zirconia-based materials.

The investigation of the ionic conductivity and cation diffusion coefficients was carried out for acid zirconium and tantalum phosphates and for series of their derivatives of composition $M_XH_{2-X}Zr(PO_4)_2.nH_2O$ and $M_XH_{1-X}Ta(PO_4)_2.nH_2O$ (where M = Li, Na). The predomination of the two-dimension bulk conductivity was established for all of these compounds. The proton mobility in solid solutions of composition $H_{1-x}M_xTa(PO_4)_2*nH_2O$ greatly exceeds that of sodium cations. Negative deviations from the additive values were observed for all conductivity dependencies on the degree of substitution. They were caused by the corporate nature of proton transport. Similar experiments for acid zirconium phosphate and its heterogeneous ion-exchange products showed that in this matrix sodium ions are more mobile than protons. The explanation for the obtained dependence of the conductivity on the degree of proton substitution was proposed. It was shown that the individual compounds with a thin layer of newly formed phase of the exchange product on the surface exhibit maximal

conductivity values. This phenomenon of sharp ionic conductivity increase was explained in terms of defect formation processes in the phase interfaces. This effect has much in common with protonic conductivity increase in hydrated zirconia.

The high-temperature solid-phase ion exchange was studied by means of thermogravimetry and X-ray powder diffraction for the systems $HTa(PO_4)_2*2H_2O$ + MCl (where M = Na, K, Rb, Cs). It was shown that ion exchange in these systems occured at 350-750^oC, after the dehydration of aqueous acid tantalum phosphate. Ion exchange processes occured in two stages for most of the components, ground together. Ion exchange initiation temperature for the first of them is lowered, and for second one - is increased with growth of the alkaline ion radius. It was established that mechanochemical interaction took place at the stage of the components preliminary mixing - while acid tantalum phosphate and alkali metal chloride are ground. Intercalation of the alkali cations in the phosphate matrix at the stage of mechanical treatment leads to the dehydration temperature increase. It also decreases the temperature of the ion exchange initiation. This effect grows stronger with intercalating cation radius increase. For the systems obtained by mixing individually ground components dehydration requires lower temperatures and ion exchange occurs in one stage at higher temperatures. So mechanochemical interaction in these systems improves thermal stability and increases ionic mobility in the matrix of acid tantalum phosphate. The estimation of the cation diffusion coefficients in the first stage products was made for the temperatures of 430, 460 and 490^oC. It was shown that the diffusion coefficient values in this temperature range increase with the increase of alkaline cation radius.

Such enhancement of ion mobility combined with the growth of thermal stability allowed us to obtain new ionic conductors based on the partially exchanged acid tantalum phosphate. Solid solutions of general formula $H_xM_yTa(PO_4)_2 \cdot nH_2O$, where *M = Cs, Ba, x = 0.50, 0.90, 0.97 and 0.99* appeared to show high protonic conductivity values (up to $5*10^{-4}$ S/cm at 600°C).

All results on the ionic conductivity are discussed using structural data for all studied substances. Different mechanisms of ion transport and defect formation in these systems are discussed.

Low temperature superplasticity of microcrystalline high-strength magnesium alloys processed by equal-channel angular pressing

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New microcrystalline magnesium alloys: MA14 (Mg – 6% Zn – 0.6% Zr; analogue of ZK60 alloy) and MA2-1 (Mg – 4% Al – 1% Zn; analogue of AZ31 alloy) are processed by equal - channel angular pressing. The record low-temperature superplastic characteristics are obtained for MA14 (elongation to failure 810% at temperature 250 °C and strain rate 3 10^{-3} s^{-1}) and for MA2-1 (elongation to failure 400% at temperature 250 °C and strain rate 3 10^{-3} s^{-1}) alloys. At room temperature elongation to failure of MA14 and MA2-1 alloys is 45% and 65%, respectively. These values exceed in 2-3 times the room temperature ductility of conventional cast and rolled magnesium alloys without decreasing tensile strength. Optimal equal - channel angular pressing regimes are developed for providing homogeneous microcrystalline structure obtaining. Microcrystalline magnesium alloys with the record superplastic characteristics has mean grain size equal to 1 □m. Optimal superplastic regimes provided maximal elongation are determined in investigated alloys. Mechanical behavior of microcrystalline magnesium alloys is investigated under conditions of low-temperature superplasticity. Dependences of superplastic flow stress, strain rate sensitivity coefficient and elongation on strain rate and temperature are investigated (tensile testing at strain rates of 10^{-4} ÷ 1 s^{-1} and temperatures of 20÷430 °C).

The model of plastic flow rheology of microcrystalline magnesium alloys at superplasticity is developed. Obtained expressions permit to calculate the dependence of flow stress (on the stage of strain hardening) on strain and strain rate, temperature and structural parameters of alloys. It is shown that unequilibrium state of grain boundaries is essential factor influence the deformation behavior of microcrystalline alloys at low-temperature superplasticity.

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Structural state of Al–Mg and Al–Zn alloys after high pressure torsion deformation

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Structural state of alloys in Al–Mg (with Mg content of 5 and 10 wt. %) and Al–Zn (with Zn content of 10, 20 and 30 wt. %) systems was investigated by means of X-ray diffraction analysis (XRDA) and transmission electron microscopy (TEM). The samples under investigation were subjected to severe plastic deformation by high-pressure torsion technique.

It was shown by TEM investigations that the deformed specimens of Al–Mg alloys had a very small grain size of about 150 nm. The presence of dispersed β-phase (Al_3Mg_2) particles detected by the additional spots in the diffraction pattern. Dislocation density was rather high; the dislocations were observed in tangles and also as subboundaries. In Al–Zn samples two types of grains were observed. The first one were of aluminium solid solution with mean size ~800 nm. The second were of Zn with mean grain size ~200 nm. Dislocation density here was lower than that in Al–Mg system.

Angle dependence of X-ray line broadening for Al–Mg deformed samples was studied and separation of contributions in the broadening due to small grain size and internal stress was performed. Mean grain size and level of elastic internal stress were respectively 112 nm, $2.6 \cdot 10^{-2}$% (for Al–5% Mg) and 125 nm, $9.9 \cdot 10^{-2}$% (for Al–10% Mg).

By XRDA we also carried out precision determination of lattice parameter both for initial and deformed material and for various concentration of the second component. It turned out that for Al–Zn system the samples after high-pressure torsion were closer to the equilibrium position than the initial ones. Behaviour of Al–Mg system was more complex. It is assumed that the insertion of big amount of vacancies in the material during the deformation leads to such kinetic conditions, which allow the system to reach the position of equilibrium.

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Accurate measurement of displacement fields by the geometrical phase method: application to dislocations, grain boundaries and small particles

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The geometrical phase method has been introduced several years ago in order to interpret in a quantitative manner the high resolution images of different crystalline defects. [1], [2]. It essentially analyses the local phase of the different Fourier components of the high resolution image. Two-dimensional maps of the displacement field around defects can then be obtained and compared to calculated models. The method is extremely sensitive to very small displacements : a hundredth of the plane spacing is easily detected. The origin of these displacements can be either structural or chemical.

Three different types of applications will be presented: isolated dislocations, grain boundaries and small particles.

The displacement field around edge dislocations is sensitive to the elastic anisotropy. It will be shown that it is possible to detect and measure this effect.

On tilt grain boundaries, the rigid body translations can be measured and the effect of the electron microscope aberration can be analyzed. As an example, the structure of the $\sum=3$ [011] (121) boundary in molybdenum is determined and compared to calculated models.

The bi-phased nano-particles can contain internal interfaces or planar defects which can be analyzed. Chemical composition gradients can also give rise to detectable effects.

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The influence of collection angle, focus and specimen thickness on the resolution and Z sensitivity in atomically resolved haadf-stem imaging

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High-angle annular dark-field (HAADF) detectors fitted in modern FEG scanning transmission electron microscopes (STEM) enable Z-contrast imaging on the atomic scale.[1,2] Such HAADF-STEM images are less dependent on focus and thickness changes compared to HRTEM images; however, recent investigations showed that this influence is significant and that image simulations are essential for correct image interpretation.[3] Until now, very few systematic experimental studies were performed to evaluate the influence of detector collection angle, focus and specimen thickness on the resolution and Z sensitivity of HAADF-STEM images. One of the reasons is that good-quality HAADF-STEM images with atomic resolution are difficult to obtain. In order to determine the optimum experimental conditions under which to obtain HAADF-STEM images, we recorded HAADF-STEM images of $CaTiO_3$ and mixed $CaTiO_3$-$La(Mg_{0.5}Ti_{0.5})O_3$ ceramics with the perovskite structure under defined detector collection angles, focus and sample thicknesses. We recorded HAADF-STEM images in a JEM-2010F microscope (c_s=0.48 mm) at inner collection angles of the annular detector from 60 to 125 mrad. The probe semi-angle was 10 mrad. The HAADF-STEM images showed that the focus value influenced both the resolution and the relative intensities between the atomic columns. The best images were recorded between the Scherzer and the Gauss focus, which was determined by image simulations. With increasing specimen thickness the intensity, signal-to-noise and also the intensity ratio between the atomic columns increased. In the thin regions of the specimen (<10nm) the existing amorphous layer greatly reduced the signal-to-noise of the image. For observed materials the best images were obtained from app. 40–50-nm-thick specimen regions. An increase in inner collection angle from 60 to 125 mrad increased the Ca/Ti and Ca,La/Ti,Mg ratio in the perovskite structure by app. 25% with a still satisfactory signal-to-noise ratio and a negligible contribution of the elastically scattered electrons. The experimental atomically resolved HAADF-STEM images were compared with simulated STEM images, which were calculated according to Bethe's method taking into account thermal diffuse scattering (TDS)[4].

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Orientation relationships and substructure of interphase boundaries in the systems Si-metal silicide films (Pt, Pd, Ni, Re, Mo, Ti, Ir)

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The crystallogeometric aspects of the phase conjugation on the interphase boundary (IB), the expected and the experimentally observed dislocation structure, the mechanism of its formation in the systems Si-metal silicide, which are characterized by different structural and dimensional misfit of crystal lattices, have been considered

1. The orientation relationships on IB are well explained within the frame of crystallogeometric criteria which are based on the CSL-lattice theory and the matching of close-packed planes across the IB.

2. Si-$NiSi_2$. In the mosaic structure of epitaxial films when the sizes of the most crystallites are commensurate with the expected period of the misfit dislocations (MD) in order of magnitude, the accommodation of misfit to the subgrains takes place and the coherent conjugation on IB within the crystallites is found. In single-crystal films the partially coherent conjugation on IB is realized. The increase in the $NiSi_2$ synthesis temperature leads to the change of mechanism for entering MD into IB, namely, the slip of the dislocations nucleated on the surface of the growing film into IB in the range of non-high temperatures (up to 700 C) and the diffusion creep in the range of high temperatures.

3. (111)Si – Pd_2Si. The dislocation structure of IB is determined by relaxation of the most dense planes of the lattices {112} and {12.0}, and the Burgers vector is dependent on the minimal vectors of the DSC-lattice with the basis vectors 1/2<110>Si (1/4<21.0> in Pd_2Si. In the case of non-crystalline silicide the interphase boundaries were not observed. This may be explained by the fact that the expected period of MD and the size of silicide grains are commensurable.

4. (111)Si-PtSi. In the system the partially coherent conjugation on IB is realized. The experimentally observed structure of IB corresponds to the rhombic network of MD with the Burgers vector 1/2<110> in Si lattice, calculated by the methods of O-lattice theory for the exact mutual orientations between Si and PtSi.

Si - ReSi. MD on IB were not revealed. The expected period of MD (both for (001)Si and (111)Si) and the silicide grain size are commensurable. This leads to accommodation of misfit on the IB and to practically coherent conjugation within each silicide grain. For the system Si-$IrSi_3$ the conjugation on IB is partially coherent, and for the same substrate temperature the mechanism for entering MD depends on the boundary orientation.

5. (111)Si - $TiSi_2$(C54), (111)Si - $MoSi_2$(T) and (001)Si - $MoSi_2$(T). In the systems with large structural and dimensional misfit the MD were not found. The plurality of orientation relationships characteristic of $MoSi_2$ and $TiSi_2$ (of both modifications) on Si rules out the possibility for the formation of single-crystal silicide films within the whole substrate surface.

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Atomic structure of symmetrical and asymmetrical tilt grain boundaries in germanium

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The bicrystal studied in the present work was prepared by the Czochralski method and was initially dedicated to grow Σ=11{233}<011>(θ=50.48°) grain boundary (GB) for its structural determination by high resolution electron microscopy (HREM). Along the Σ=11 GB, we observed two interface types: a symmetrical one parallel to $\{233\}_1//\{233\}_2$ planes and an asymmetrical one parallel to $\{144\}_1//\{522\}_2$ planes. The symmetrical part has been extensively studied in the past [review paper 1, 2]. Since this Σ=11 GB has a high energy, it spontaneously dissociates into two GBs: a very simple Σ=3{111}<011>(θ=70.53°) twin GB and a Σ=33<011>(θ=20.05°) GB. Furthermore, two types of Σ=33 interfaces are actually observed, a symmetrical part parallel to $\{144\}_1//\{144\}_2$ planes,), and an asymmetrical part parallel to $\{111\}_1//\{5\ 13\ 13\}_2$ planes. HREM was carried out using a JEOL 4000EX electron microscope.

It will be shown [3] that the structure of the simple symmetrical GB Σ=33{144}<011> (θ=20.05°) has a glide mirror symmetry and is different from model previously calculated where a mirror symmetry was expected. New numerical simulations performed either for Ge or Si with different types of potentials sustain our model. The structure of the asymmetrical parts of the GBs have been studied and also compared with previous studies on an asymmetrical Σ=9 GB [2]. Our results show that the asymmetrical grain boundaries have high energies compared to symmetrical ones. This study of several asymmetrical GBs of the <011> family shows that they have common structural features, especially the stable structure leads to a surface maximization involving a {111} plane of an adjacent grain. This kind of configuration is obtained by micro-dissociation. Also we note that the atomic structure of asymmetrical GBs are not made with new structural units: it is made of the SUs appearing in the symmetrical constituting GBs.

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TEM studies of grain boundaries in the Al(Ga) system and in $SrTiO_3$

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Probably the most prominent effect of material embrittlement occurs in the Al(Ga) system. Despite this startling effect, very little is known about this process on the atomistic level. We will report on the segregation behaviour of Ga to Al grain boundaries. This was studied by analytical transmission electron microscopy (AEM). In addition high-resolution TEM results will be shown which may clarify the influence of Ga on the GB migration.

In $SrTiO_3$ we investigated small angle GBs by AEM and high-resolution TEM. From these results we obtain information about the electronic and atomistic structure as well as the chemistry of individual dislocation cores. The implications of the results to the plasticity and electronic transport properties in $SrTiO_3$ will be discussed.

Determination of the force constant in the near-surface region using LEED

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The method of the non-destructive layer-by-layer analysis of the distributions mean-square displacements (MSD) of atoms, Debye temperature and force constant in the near-surface region by width in some interplanar distances is suggested. The method based on determination of the energy dependencies MSD of atoms applying low-energy electron diffraction (LEED) and consequence of its mathematical treatment for layer-by-layer restoration of information, using singular value decomposition (SVD) algorithm. Applying know tight-relation between its values and MSD of atoms the calculation of layer-by-layer Debye temperatures and force constants was produced. Its numerical values for five layers of near-surface region of alloy $Co_{50}Ni_{50}$ with orientation of (110), (100) and (111) are obtained. The observable orientation anisotropy of a force constant well correlated with a modification of a coordination number and amount of the dangling bonds for the surface atoms. It is shown, that the force constant, per one bond and skin depth for (*hkl*) face versus reticulate covered density of surface has power law. The energy of interatomic interaction in the surface layers essentially differ from those in bulk single-crystal has been found.

TEM and OIM study of grain boundaries in recrystallized nichrome

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Last decade a considerable interest has been drawn to grain boundary engineering (GBE), a possibility to modify physical and mechanical properties by alteration of grain boundary misorientation distribution (GBMD). Results of intensive study of GBMD by means of transmission electron microscopy (TEM) and Orientation Imaging Microscopy (OIM) provide not only an information on processes occurring in polycrystals during plastic deformation and recrystallization but also give a possibility for future technological applications of GBE.

This paper presents the results of experimental studying of GBMD evolution during annealing in nichrome (80%Ni-20%Cr), which possesses the mild energy of stacking fault. TEM and OIM were used in the study. Two different states of Ni-20%Cr alloy were produced by cold rolling and following annealing: the sample (a) was obtained by cold rolling at room temperature with total reduction in thickness of 70% and by annealing in salt bath at 993 K for 2 hours. The sample (a) underwent a primary recrystallization that led to the microstructure with a mean grain size of about 6 μm and low dislocation density. The sample (b) was obtained by additional annealing at the temperature 1273 K for half an hour. This heat treatment gives the microstructure with a mean grain size of about 13 μm that is evidence for normal grain growth occurred in the alloy. Using TEM diffraction methods and orientation electron microscopy grain boundary misorientation distribution has been measured and compared in the both samples. The analysis of results obtained shows that a decrease in the free energy of GBs occurs by an increase of total length of special grain boundaries having low surface tension energy, by a decrease of total deviation of GBs from precise CSL misorientation and by a decrease of total length of high-angle random boundaries. It can be concluded that two mechanisms of GBMD formation during annealing operate in Ni-20%Cr alloy, namely multiple twinning and dissociation of high-angle random boundaries.

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Discontinuous dissolution of ZrO_2-Y_2O_3 columnar crystals

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Thermal barrier coatings in heat and gas turbines, aircraft and high-compression engines should be resistant to service temperature as high as 1800 K. Such barriers can be obtained using plasma spraying. The technique involves short time of high temperature action and subsequent high cooling rate of the target particles when touching substrate surface. This favors a formation of transition phases rather than the equilibrium ones. However, the resulting inhomogeneity and thermal strains require further annealing.

In the present paper, scanning and transmission electron microscopes equipped with attachments for X-ray microchemical analysis, and X-ray diffractometry were applied for the studies of the ZrO_2+20 wt.% Y_2O_3 target which was plasma sprayed on a Ni-base substrate The plasma spraying leads to a rapid crystallization of the target and formation of the columnar crystals localized within colonies 5 μm in size, separating from the equiaxed grains of the matrix phase by high-angle boundaries. The columnar crystals can be treated as a separate phase (of a cylindrical shape 1 μm in diameter). Both phases are of regular symmetry with different lattice parameter. They are not in the equilibrium state because their compositions correspond to the retrograde solidus (columnar crystals) and liquidus (matrix phase) lines in the equilibrium phase diagram given by Levin and Mc Murdie [1].

During subsequent annealing at 1220 K the boundaries of the colony containing the columnar grains were observe to migrate backward towards the center of the colony leaving behind a new near-equilibrium phase. Such a mechanism, observed for the first time in this kind of ceramic materials, is similar to the discontinuous dissolution of two-phase lamellar structure in metallic alloys [2]. On the other hand, an example of eutectoid decomposition of a supersaturated solid solution in ZrO_2+MgO ceramics resulting in the formation of colonies of the two-phase lamellar structure was described by Czeppe, Zięba and Pawłowski [3]. Both processes are governed by diffusion at the colony boundary where a sharp change of chemical composition and crystal orientation are also detected.

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Interphase interaction of Zr-based alloy with refractory materials

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Zr-Cu based alloys are interesting both for practical application and for theoretical aspect. They can bee used as the superconductors, amorphous materials, solders and shape-memory materials. The malting of Zr-based alloys on air have so-me difficult: chemical composition of alloys can be changed, the materials of cru-cible can be destructed. That is why the wetting of some refractory materials with Zr-Cu-Ni-Al alloys have been studied. Iodic zirconium, copper of type M0 (99.95%), nickel of type N0 (99.985%), aluminium (99.99%) were used for the preparation of Zr-Cu-Ni-Al alloys.Al_2O_3, Y_2O_3, SiO_2, Al_2O_3-MgO-Cr_2O_3, ZrO_2-CaO-SiO_2, AlN, BCN were used as the refractory materials. The research of interphase properties of Zr-based alloys – refractory material system were studied by the method of sessile drop. It was done in vacuum ($2.266*10^{-5}$ Pa.) within the range of temperature from 920 to 1200°C. It was fixed that the den-city and the surface tension of liquid Zr-based alloy are described by next empirical equation:

$$\rho = 5.71 - 0.013\ (t - 920) \quad (1)$$

$$\sigma_{lg} = 1527 - 0.15\ (t - 920) \quad (2)$$

where t – temperature, °C

It was fixed, also, that with increasing of temperature and time of contact the decrease of wetting angle is observed for all systems.

Only when temperature is 985˚C the wetting angles is less then 90grad. Heat time of liquid alloy on ZrO_2-CaO, Al_2O_3 refractory materials at this temperature during 10min. and 40min. leading to decrease of wetting angles down to 55grad. and 30 grad. consequently. The data of wetting of Y_2O_3 and SiO_2 by Zr-based alloy are di-ffer from all others. The Y_2O_3 and SiO_2 refractory materials are wetted at 1100˚C and 1020˚C consequently. Decreasing of interphase tension and increasing of chemical interaction on the interface liquid alloy – refractory materials are cause of increase the wetting when the temperature and time of contact are increase.

Zirconium is very chemically active element. That is why it reduces almost all oxides. Due to difference between diffusion velocity of oxygen and such elements as Al, Mg, Y etc oxygen desolves in crystallographic lattice of Zr, and reduced elements mainly concentrate in interaction zone, that is to say, on the interface solid – liquid. Also formation of chemical bond metal – oxygen in zone of contact with the help of surface oxidation is enable. After formation of this bond interaction of oxide's coatings of metal and oxides that is to say, with stabilized additives of investigated ceramics is observed. These coatings are bound with strong ionic bond with anion of solid oxide, building its lattice. Ions of oxygen from the liquid metal concentrate on these positive – charged points (cations of metal). It leads to formation of complex oxides of liquid phase.

Grain boundary precipitation in ferritic steels

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A new model for grain boundary precipitation is described. It uses a Monte Carlo approach and has been shown to be very successful in predicting chromium carbide, MX and Laves phase precipitation in ferritic stainless steels. The total precipitation picture can be presented at any time as a function of temperature.Segregation, nucleation, growth, and coarsening are all automatically included in the model.

Faceting–defaceting transition in Σ5 (310)[001] grain boundary of $SrTiO_3$

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Using high-resolution electron microscopy (HREM), temperature dependence of faceting of an asymmetric Σ5 grain boundary (GB) in $SrTiO_3$ is observed [1]. The bicrystal samples have been fabricated by ultra-high vacuum diffusion bonding and heat-treated between 1100^{o}C and 1600^{o}C. Below 1300^{o}C, this GB facets into symmetric GB (310) and asymmetric GB (100)//(430) planes. At 1300^{o}C, in addition to the asymmetric facet, the symmetric {210} facet appears: Three different facets are thus observed at this temperature. At 1400^{o}C and 1500^{o}C, the asymmetric facet disappears and the two kinds of symmetric facets remain. At 1600^{o}C, faceting disappears and the GB becomes defaceted. The gradual change of the defaceting transition between 1500^{o}C and 1600^{o}C is presented [2]. The faceting/defaceting transition behavior of the GB is interpreted in terms of the Wulff plot and its corresponding equilibrium crystal shape.

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Wetting of nitride ceramics by Cu- and Ag-based reactive alloys

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Behavior of nitride ceramics in contact with molten alloys is interesting for two kinds of applications. First the use of nitride ceramics as tooling materials in manufacturing metal alloys and second to join these materials together by brazing alloys. Key parameters for these applications are wetting and adhesion. Both wetting and adhesion depend strongly on reactivity.

In this work wetting (spreading rate and final contact angles) of polycrystalline AlN and Si3N4 substrates by CuZr, CuCr and AgZr alloys are studied by the sessile drop method at 1373 K. Experiments are done in high vacuum to minimize the oxidation of reactive alloying elements Cr and Zr. After the equilibrium contact angle is achieved the sample is let to solidify. Droplet adhesion to the substrate and possible cracking from thermal stress in the sample are examined. Drop / substrate interface morphology and chemistry are characterized from a crosscut by scanning electron microscopy and X-ray microanalysis.

Experiments are performed using different alloy/ceramic combinations in order to study the effect on wetting and adhesion (i) of reactive alloying element (Cr or Zr) (ii) of metal matrix (Cu or Ag) and (iii) of nitride ceramic (aluminum or silicon nitride).

Influence of Bi on faceting of Σ3 and Σ9 grain boundaries in Cu

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Thermal groowing is a diffusion-controlled process, which allows to measure the contact angle at the intersection of an interface (grain of interphase boundary) with a free surface. Such data deliver the values of interface energy (exactly speaking, the ratio between energies of an interface and a surface). Unfortunately, with decreasing tempertature or interface energy the depth of the groove developed in the reasonable time decreases drastically. Recent development in the atomic force microscopy (AFM) increased the accuracy of the contact angle measurements and allowed the exact investigations of very shallow grooves. In such a way the investigations of the grain boundary (GB) phase transitions were performed.

Faceting is a well documented phenomenon known both for surfaces and interfaces, particularly, grain boundaries. 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 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). In most cases the GB facets lie in the CSL planes with high density of coincidence sites. For the investigation of GB faceting a cylindric Cu bicrystal with an island grain was grown with the aid of the Bridgman technique from Cu of 99.999 wt.% purity. Various concentrations of Bi were obtained by alloying form the gas phase. Grain *1* in this bicrystal is completely surrounded by grain *2* forming the Σ9 <110>tilt GB. The faceting was analyzed in an *as-grown* bicrystal and after annealing at 1020 °C. The dissociation $\Sigma 9 \rightarrow \Sigma 3 + \Sigma 3$ proceeds in our samples. The twins appear during the growth of the bicrystal instead of $\{111\}_1/\{115\}_2$ or $(110)_{\Sigma 9CSL}$ facet. The profiles of the formed GB thermal groove were analysed with the aid of AFM. With increasing Bi concentartion the GB groove deepens drastically. Wulff-Herring plots and GB phase diagrams have been constructed for the Σ3, Σ9 and Σ9+Σ3 GBs at three concentrations of Bi.

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Influence of Bi on faceting of Σ3 and Σ9 grain boundaries in Cu

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Grain boundary wetting and premelting phase transitions in the Mo–Ni system

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Liquid phase sintering is widely used for manufacturing of parts made from refractory alloys because the addition of metals with a lower melting temperature like Ni or Cu enhances drastically the consolidation process of Mo or W. In fact, the behaviour of liquid phase sintering depends critically on the competition between the diffusional and non-diffusional processes, like grain boundary (GB) migration, liquid film migration, and GB penetration of a liquid phase. The last process can proceed only if the dihedral contact angle in a triple point "GB – two solid/liquid interphase boundaries" $\theta = 0$. The temperature T_w can exist such that for $T > T_w$ the contact angle $\theta = 0$ and for $T < T_w$ $\theta > 0$. Above this temperature the GB is completely wetted by the liquid phase and penetration can occur, while at lower temperatures the wetting is incomplete and the liquid films along the GBs are not formed. This change at T_w has a name of GB wetting phase transition. The value of T_w is governed by the ratio of energies of GB and solid/liquid interphase boundaries. Above T_w GB cannot exist in the equilibrium with a liquid phase which must separate the individual solid grains. The behaviour of the liquid phase sintering has not been treated so far from the viewpoint of GB wetting phase transitions. This is due to the lack of information about the temperature dependence of the GB dihedral contact angle. T_w depends essentially on the GB energy. Therefore, the dependencies θ (T) should be measured with the aid of individual GBs in bicrystals. Two [110] cylindric Mo bicrystals were grown in the vacuum floating zone melting apparatus from Mo of 99.95 wt.% purity. Tilt symmetric [110] GBs have the misorientation angles of 20° and 70°. The bicrystalline platelets and the polycrystalline foil covered by nickel were that positioned on the sample holder made of ø1 mm 99.9 wt.% Mo wire and annealed in the temperature interval from 1200 to 1780 °C. The contact angles were measured for both Mo bicrystals, polycrystalline Mo foil and polycrystalline Mo wire. The angle θ and for bicrystals and mean values of θ for polycrystals decrease gradually from 180°C down to 0° with increasing temperature. It means that the GB wetting phase transition proceeds in the Mo–Ni system. Above 1360 °C all GBs are wetted by the melt. The grains in the Mo foil are completely separated from each other. First completely wetted GBs appear already at 1320 °C. The lines of the GB wetting phase transition were constructed in the bulk Mo–Ni phase diagram. The influence of the GB wetting phase transitions on the liquid phase sintering and semi-solid processing is discussed.

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Grain boundary faceting phase transitions at the twin boundaries in Zn

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Faceting is a well documented phenomenon known both for surfaces and interfaces, particularly, grain boundaries (GBs). 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 be observed 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). In most cases the GB facets lie in the CSL planes with high density of coincidence sites. Zn **Ошибка! Закладка не определена.**$[11\bar{2}0]$ flat single crystals were grown using the modified Bridgman technique from Zn of 99.999 wt.% purity. Individual elongated twin plates having very uniform thickness were produced with the aid of slight deformation of single crystals. The produced twin plates are perpendicular to the surface of the sample and possess a very uniform thickness. The **Ошибка! Закладка не определена.**$[11\bar{2}0]$ axes in both grains are also perpendicular to the surface of the sample. The parallel long sides of the twin plate are formed by the symmetric twin GBs or $(100)_{CSL}$ facets. Due to its optical anisotropy, zink allows one to study the shape of the GB with the aid of polarized light. The stationary shape of the slowly migrating tip of the twin plate has been studied *in situ* in the hot stage of optical microscope in the temeparature interval from 317 to 417 °C. It has been shown that below 357 °C the twin tip contains only one plane facet, namely asymmetric twin GB $(010)_{CSL}$. The $(010)_{CSL}$ facet has the angle of about 86° with the symmetric twin $(100)_{CSL}$. Above 357 °C the second facet $(110)_{CSL}$ appear at the tip of the twin plate. The second $(110)_{CSL}$ facet in the twin tip has the angle of about 45° with the symmetric twin $(100)_{CSL}$. By temperature increase from 357 to 412 °C the length ratio of $(010)_{CSL}$ and $(110)_{CSL}$ facets increases from 0 to 1. Above 412 °C only one $(110)_{CSL}$ facet is present in the twin tip. The indications of the GB roughening phase transition were also observed, namely the corners of the facets become smoother with increasing temperature. The GB phase diagram for the twin GBs in zink containing the lines of GB faceting and GB roughening phase transition has been constructed. In it has been previously shown that the GB possess the special structure and properties in the limited areas of temperature T and misorientation θ close to a coincidence misorientation θ_Σ. In other words, by increase of $\Delta\theta = |\theta - \theta_\Sigma|$ and T the phase transition „special GB – general GB“ proceeds and GB looses its special structure and properties. The ratio of a and c spacings in Zn is not rational and is temperature dependent. Therefore, the GB $(010)_{CSL} \rightarrow (010)_{CSL} + (110)_{CSL} \rightarrow (110)_{CSL}$ GB faceting transition can be driven by the c/a temperature dependence of the constrained CSL structure.

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Grain boundary wetting by liquid phase in the Zn–Al system

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If we consider the equilibrium contact between grain boundary (GB) in the solid polycrystal and melt in thetwo-component system, the temperature T_w can exist such that for $T > T_w$ the contact angle $\theta = 0$ and for $T < T_w$ $\theta > 0$. Above this temperature the GB is completely wetted by the liquid phase, while at lower temperatures the wetting is incomplete and the liquid films along the GBs are not formed. This change at T_w has a name of GB wetting phase transition. The value of T_w is governed by the ratio of energies of GB and solid/liquid interphase boundaries. Above T_w GB cannot exist in the equilibrium with a liquid phase which must separate the individual solid grains.

Zn **Ошибка! Закладка не определена.**$[11\bar{2}0]$ flat bycrystals with tilt GBs were grown using the modified Bridgman technique from Zn of 99.999 wt.% purity. Three different GBs were grown: (1) with low energy and misorientation angles 11.5º (low-angle GB), with high energy and misorientation angle 46º and high-angle low-energy twin GB with misorientation angle 84º. The bicystalline samples were coated with a layer of Al-Zn mixture and annealed in the two-phase area of the Zn–Al wher the solid (Zn) phase is in equlibrium with (Al) melt. The contact angles were measured after quenching and sectioning on the ground and polished surface. The GB wetting phase transition was observed in all GBs studied around 418ºC. Previously, the observed temperature dependence of the contact angle were always convex, and the break of the temperature derivative of contact angle was always observed. It means that till now only the GB wetting phase transitions of the first order were observed. In the Zn–Al system all three temperature dependences are concave and no observable break of the temperature derivative of contact angle is present. Therefore, the GB wetting phase transitions of the second order is observed for the first time.

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Grain boundary wetting by a solid phase in the Zn–Al system

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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 a Zn-5 wt.% Al alloys, which were annealed at several temperatures in the range of two solid phases (523–648 K). 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 a 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 number of (Zn)/(Zn) GBs covered by this layer decreased, and 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.

Grain boundary wetting phase transitions in the Al–Zn system

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Grain boundary (GB) phase transitions can change drastically the properties of nanograined polycrystals, leading to enhanced plasticity or brittleness, increasing diffusion permeability, they influence also liquid-phase and activated sintering, soldering, processing of semi-solid materials [1–3]. GB wetting phase transition can occur in the two-phase area of the bulk phase diagram where the liquid and solid phases are in equlibrium. Above the temperature of GB wetting phase transition a GB cannot exist in equlibrium contact with the liquid phase. The liquid phase has to substitute the GB and to separate both grains. In case if two solid phases are in equilibrium, the layer of the second solid phase can substitute the GB and "solid state wetting" (covering) occurs. In this cas the layer of the solid phase *2* has to substitute GBs in the solid phase *1*.

Al <110> flat bycrystals with tilt GBs were grown using the modified Bridgman technique from Al of 99.999 wt.% purity. Three different GBs were grown: (1) with low energy and misorientation angles 15º (low-angle GB), with high energy and misorientation angle 35º and high-angle low-energy twin GB with misorientation angle 70.5º. 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 equlibrium with (Zn) melt. The contact angles were measured after quenching and sectioning on the ground and polished surface. The GB wetting phase transition was observed in all GBs studied. The observed temperature dependence of the contact angle is convex, and the break of the temperature derivative of contact angle is also observed. It means that the GB wetting phase transition in the Al–Zn two-phase area is of the first order, unlike to the Zn–Al two-phase area, where it is of the second order.

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Contact force measurements in the interface of two solids

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The nanotechnology is a new field in material science, biotechnology, computer and another modern technologies. The manipulation of nanometer size objects is a gate to design of new miniature sensors, actuators, micro robots and nano computers. Such a manipulation needs a measurement of nano scale friction, adhesion and surface properties of materials.

Realization of MEMS and similar products needs a precise control of all of forces acting in the interface of parts of the nano and micro objects as during assembling as in operation. It is well known that the surface and interface forces play dominant role in nano scale. Most problems in miniaturized and precise devices arise from the unknown adhesion between their parts. Another problem is the analysis of the interface forces in composites and coated solids, especially when the thickness of coatings is in micro and nano scale.

The paper presents the data on measurements made using the device designed in MPRI to investigate contact forces in the interface of solids in the range of 10-10000 μN. The device consists of ball probe with diameter 0.5-10 mm fixed on the arm of high sensible electromagnetic balance with negative feedback. The test sample is approached to the ball up to the predefined contact force (10-10000 μN). The dependence of adhesion forces vs distance between ball probe and sample is measured at approach and pull-off the sample from the ball. The interface forces tended to rotate the arm with ball are compensated by electromagnet located on the opposite arm of the balance. The measurement of compensative current in the electromagnet allows us to define the acting interface forces. The sample movement is realized with piezo-stack and can be varied from 0.1 to 10 nm/s. in the range up to the 10μm.

The results of investigation of different thin coatings and self-assembled monolayers are presented and discussed. It is shown that these results are strongly dependent on the ambient conditions.

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Interface reaction in diffusion-soldered Cu/In-48Sn/Cu joints

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This work describes a Pb-free solder alternative for the interconnection technology and its implementation in a diffusion soldering technique: In-48at.%Sn solder (eutectic alloy) , with a melting point of 120°C. The system proposed has the advantages of both traditional soldering and diffusion bonding, i.e., good joint filling, high service temperature, and good mechanical properties. The diffusion reaction processes in Cu/In-48at.%Sn/Cu joints were investigated between 180 and 400°C. Electron microprobe analysis revealed the presence of one or two intermetallic layers in the interconnection zone: a layer of the η phase below 200°C, and layers of the η and ζ phases above 200°C. The η and ζ phases form through a solid-liquid and a solid-solid diffusion reaction, respectively. Below 200°C the η phase exhibits two different morphologies: large coarse grains at the η/(originally liquid)In-48at.%Sn interface and a fine-grained region at the Cu/η interface. The thickness of the ζ layer shows a constant growth rate (linear growth) at constant temperature. The temperature dependence of the growth rate constant of the ζ layer is described by an Arrhenius relationship with an activation energy equal to 121 kJ/mol and a pre-exponential factor of about 57 m/s.

Interaction of high-current fluxes of nitrogen ions with various metallic substrates

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Interaction of high-current fluxes of carbon and nitrogen ions with various metallic substrates

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Intercation of ionic fluxes with metallic substrates play an important role for the surface modification of materials. Particularly, in case of metallic substrates the carbon diffusion into the substrate during the deposition and during the life-time of the coated part can deteriorate drastically its properties. The results of ionic nitriding are also controlled by the ballistic and diffusional penetration of nitrogen into metallic substrates. For the deposition of diamond-like coatings and ionic nitriding the novel industrial vacuum arc apparatus «Nikolay» was used which allows one to coat the large area parts with dimensions up to 2100x1400 mm. This apparatus comprises the novel Hall current accelerator for ionic cleaning and implantation of substrates. The accelerator has a large aperture of 1400 mm and a power up to 10 kW. High ionic currents up to 1 mA/cm^2 permit to use the source both for ion implantation and for ionic cleaning of substrates. Various gases can be used for both purposes: argon, nitrogen, oxygen, etc. The ionic nitriding of austenitic stainless steel and ferritic low-carbon steel has been studied. The diamond-like coating was deposited simultaneously in the identical conditions on the polished substrates of polycrystalline austenitic stainless steel (with fcc structure), ferritic low-carbon steel (with bcc structure), copper and (for comparison) on silicate glass. Depth profiles of carbon and nitrogen measured with the aid of secondary-ion mass spectroscopy are presented. The temperature dependences in Arrhenius coordinates for the effective diffusion coefficient of carbon and nitrogen into of austenitic stainless steel and ferritic low-carbon steel were obtained. They are discussed using the hypothesis of the grain boundary phase transformations in steels. The financial support of Russian Foundation for Basic Research and the Government of the Moscow district (contract 01-02-97039), NATO Linkage grant (contract PST.CLG.979375) and Royal Swedish Academy of Sciences (cooperation program between Sweden and the former Soviet Union) is acknowledged.

Preparation of Nb/Ni nanoscale layered system with smooth interface

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Recently much attention has been paid to prepare Superconductor/Ferromagnet (S/F) layered systems for spin polarized transport experiments and further application such systems for magnetoelectronics [1]. One of the difficulties rose in such experiments is roughness of the S/F interface. In present work we developed DC-magnetron deposition process for preparation of Nb/Ni bilayers with very smooth interface. The quality of the surface and S/F interface for prepared nanoscale layered samples was investigated by θ-2θ X-ray small angle diffractometry ($2\theta < 10^0$, CuK_α radiation) and demonstrated well resolved oscillations of the reflectivity as a function of angle, weakly damped in more than 5 orders of intensity. A quantitative analysis of the X-ray data in frame of the Parratt formalism [2] gives the value of the layers roughness σ_{rms} less than 0.3 nm.

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About a surface of high-dispersed powders on a basis of intermetallic compounds of samarium

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The dispergation process, alongside with process of the subsequent sintering, is one of the basic stages of obtaining constant magnets. In this report we present the results received at research of dispergation process of the intermetallic compounds of samarium ($SmCo_5$ and Sm_2Fe_{17}) at their treatment by ammonia in the presence of ammonium chloride as reaction promoter. The influence of nitriding temperature (150-300°C), of ammonia pressure and a number of sorption-desorption cycles on a dispersion of formed powders is investigated. The ammonium chloride and the chlorine-containing products of nitriding are removed by washing by ethanol and water. It is shown, that at heating of a reaction mixture up to 200°C the atoms of not only hydrogen, but also nitrogen, generated by ammonia, will penetrate into a crystal lattice of the intermetallide, that results in a formation of the powders of the appropriate hydride-nitride phases. The magnitude of a surface of nitriding products rises on the order above of appropriate value for initial intermetallides (7.8 m^2/g against 0.1 m^2/g). The intermetallide interaction with ammonia at 300°C and above is accompanied by a destruction of a metal matrix. The magnetic properties of the products of intermetallide nitriding received at 200°C are investigated. The established high enough value of a coercivity of nitriding products confirms the introduction of nitrogen atoms into a crystal lattice of the intermetallide.

The peak with m/z = 18 is by the most intensive peak on a mass-spectrum of gas assembled above the powders of the intermetallic compounds of samarium at their heating up to 300°C. The appearance of this peak is caused by molecules of water. At a spectrum also there are intensive enough peaks with m/z = 44 and 28. The first peak can be connected with presence of CO_2 at a gas phase, and the peak with m/z = 28 – with N_2 or CO. The presence of the nitrogen-containing compounds at a spectrum does not cause doubt, as the intensity of peak with m/z = 17 essentially exceeds those in the case of a spectrum of pure water. The peak with m/z = 31 is probably caused by the residues of ethanol, which was used at washing a sample.

Thus, the carried investigations have shown, that the surface of the high-dispersed powders of the intermetallic compounds of samarium, obtained with use of the ammonia and the ammonium chloride during refining, besides of adsorbed molecules of water, contains some of technological impurity. This fact is necessary to take into account at the subsequent stages of a processing of the powders in constant magnets, when the external borders become by the internal one.

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Formation of nanocrystalline layer substructure in highly-doped silicon films

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In the paper the layer grain substructure of polycrystalline highly As-doped silicon films is investigated, and the mechanism of its formation is discussed. The Si-As films were growth by pyrolysis of silane on different substrates (SiO_2, Si_3N_4, Si) with the presence of the volatile component (AsH_3) in the gaseous phase. The deposition rate of the film was about 5 nm/s. In all the experiments the concentration of the volatile gas impurity (AsH_3) was kept constant (2.5%) with respect to the main reagent (SiH_4). The electron microscopic investigations of he films have shown that the grains have a layer substructure. The layer boundaries were along (111) planes normal to the substrate. The layer width increased with the increase of the growth temperature from 5 nm (800^0C) to 80 nm (1050^0C).

It is suggested that the main process determining the formation of such layer structure is the diffusion process of silicon and arsenic atoms on the surface of the substrate and the growing grains. At the initial deposition stages the separate silicon grains grow at the expense of the lateral atom flux over the substrate surface, and the grain side is a close-packed plane (111) on which the impurity (As) is gradually accumulating. At some time the Si-atoms form (111) plane of a new layer. After the grain grow to getter to form a continuous film, the formation of the structure occurs as a result of diffusion over its surface. During pyrolysis of silane the As-atoms, falling on the surface of the formed Si-layers, diffuse to As-interlayers between them. The silicon atoms embed in their crystal lattice. Thus, the growth of Si and As layer continues in vertical direction.

To quantitatively describe the formation kinetics of vertical layer substructure, the equation of surface diffusion for As-atoms is solved, with the fact in view that the boundary of Si-grain is an infinite grain for As-atoms. It is shown that for the experimental deposition parameters the impurity atoms on the surface of silicon grains do not exceed one monolayer for the values of activation energy of surface diffusion E_d lower than 2.15 eV. Since the real values of Ed (As) for Si do not exceed this value, the surface of Si-grain will be clearing from the alloying impurity during the period of the film growth.

The analysis of dependence of Si layers width on temperature shows that along with the diffusion accumulation of impurity on the growth front the width of Si layers may be controlled by the surface diffusion of silicon atoms.

During the growth of polycrystalline As-doped silicon films the layer substructure of the grains is formed, the nature of which is connected with impurity segregation on the front of the grain growth, which leads to blocking of the growth and subsequent nucleation of a new layer. The activation energy for the surface diffusion of the alloying impurity below which the layer substructure of the grains is realized, has been determined.

Expert systems for predicting optimal orientation relationships in heterosystems on interphase boundary

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The properties of the materials in which the fraction of the interfaces is comparable with the volume fraction of the crystallites (in particular, multiplayer film compositions) are mainly dependent on the interfaces properties, which are dependent on the boundary structure, i.e. on their orientation and orientation relationships (OR) between the phases.

For the complex crystal lattice the only method to predict optimal OR on the interphase boundary (IB) is based on the common crystallogeometric criteria of phase conjugation. The main of them are as follows: 1) parallel conjugation of crystal lattices or parallelism of close-packed directions; 2) realization of close-packed coincidence site lattices on the IB; 3) good matching of close-packed planes on the boundary; 4) approximately the same densities for the atoms in the planes of each crystal on IB; 5) the tension of the forming film is more preferable then compression.

Among the different orientation relationships the optimal OR will be the one for which the majority of criteria is fulfilled. The analysis of all the possible OR is rather complicated. Besides, the problem is that for the criteria a qualitative estimation is used, and the question of priority ("specific weights") for these criteria have not been solved.

The development of expert systems (ES) to predict the optimal orientations is the solution of this problem. The aim of the present work is to determine the main trends for the development of such system and its structure.

First of all the ES should be able to execute all the routine work to find the OR, which involves determination of coincidence sites, matching of the planes, comparison of atomic densities for different boundary orientations. As a result, the list of possible orientations for the boundary plane with a set of azimuthal orientations, taking into account the criteria 2 – 4, will be made. This task is realized by the calculation block of the ES.

The next task is the analysis of OR and the choice of optimal OR. For this purpose the criteria should be formalized, i.e. one must go from the qualitative estimation to the quantitative one. The method to calculate the numerical parameter for each criterion should be found. The priority ("specific weights") of the parameter and also the criteria 1, 5 should be taken in to account. The estimations based on the analysis of the experimentally observed OR are necessary to fulfill this task.

The ES to predict the OR for the simplest case of conjugation of fcc crystals has been developed. The choice of the possible structures is limited by a great number of experimental results for such heterosystems, which allows to improve the methods for the quantitative estimation of the criteria and to determine their priority.

The ES is in good agreement with the experimental results and is very promising.

Grain growth in Ag films

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The purpose of my work is an attempt to find the dependence the evolution of microstructure in microcrystalline films during normal grain growth on grain size.

Ag 99.999% was chosen as a material for experiments. Microcrystalline 1000 Å film, nontextured, were produced by vacuum evaporation on glass substrate with a sugar sublayer. In order to obtain a homogeneous microcrystalline structure the substrate temperature was maintained at 100°C. The mean grain size was 200-400 A. The microdiffracton pattern of these films showed that the intensity of rings corresponds to randomly oriented grains.

Free thin films were annealed in a specially designing furnace in vacuum, the temperature being maintained up to 1°C. Heating and cooling up to the required temperature took a few seconds. The film were investigated in TEM on special supporting nets. Dark-field TEM based technique was used for the grain size measurements. The dark field image is formed by deflecting electronic beam to different reflections and shows which grains contribute to a diffracted beam. The mean grain size measurement was made twice on each film: before and after isothermal annealing. The annealing were done at 300 - 600° C ,since it is known that at 700°C secondary recrystallization takes place. Grain size growth increases at 300°C already. The grain size is changing mainly at 400 - 500°C. The grains have equilibrium shape. At T=500-600°C the mean grain size becomes more than film thickness. The relative grain size distribution is steady-state within experimental error after annealing 1-5 hours. The time dependence of mean grain size for different annealing temperatures may be written by parabolic law. We investigated more carefully the initial section of the mean grain size time dependence and we found that it exhibit linear time dependence. We suppose linear time dependence is due to triple junction drag of the boundary motion.

We investigated the rate of change of mean grain size on the initial grain size. At low temperatures (300-350°C) there are no difference in rate of mean grain size with increasing of initial grain size. It means that triple junction migration is main process in grain growth. With the increasing temperature the rate of change of mean grain size increases. We suppose in some parts of microstructure the migration of grain boundaries comes into force. The higher temperature the more effect of grain boundary migration. The experimental results provide support for this view.

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Atomic simulation of [001] tilt grain boundaries in Ni and Cu

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In the present work molecular statics simulations of the atomic structure of symmetrical [001] tilt grain boundaries (GBs) in Ni and Cu have been carried out. The simulations have been done by the use of DYNAMO codes, which uses the embedded atom method (EAM) [1]. The EAM potential have a significant advantage over pair potentials, since it includes in an implicit way the many-body effects and is much more reliable in the simulations of various defects. The simulation cell contained two parallel GBs with the same but opposite misorientations having an identical structure, which are separated by a distance sufficient to exclude their interaction. Periodic border conditions have been applied in all three directions, with fixed borders perpendicular to the GB plane and dynamic borders parallel to the GBs so that simulations were performed under constant zero pressure.

The GB structures and energies in Ni and Cu have been calculated for the whole misorientation range. Taking the energies of two $\Sigma=5$ GBs as input, the energy versus misorientation angle curves were calculated by the use of disclination structural-unit model [2] and a nearly ideal fit to the simulation results has been obtained. The stability of two type structures for GBs $\Sigma=5/36.87°$ (B and B′) and $\Sigma=5/53.13°$ (C and C′) reported earlier on the basis of pair potentials [3] has been studied under the constant pressure and constant volume conditions. In Ni the B structure of $\Sigma=5/36.87°$ GB is unstable at any condition. However, the GBs from the range $36.87° < \theta < 53.13°$ can have a metastable structure with B units. A transition from the non-stability to the metastability of such structures occurs at about $\theta \approx 45.6°$ for constant pressure and $\theta \approx 43.5°$ for constant volume.

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Asymmetric grain boundaries in elemental semiconductors and metals. Atomistic simulations and observations

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We present a parallel of recent studies at the atomic level of asymmetric tilt grain boundary (ATGB) structures in elemental metals and semiconductors using high resolution transmission electron microscopy observations of real systems sustained by atomistics simulations. The {111} // {13 13 5} and {111} // {331} ATGBs, where one of the two planes is the privileged (111) plane, will be presented first. The {441} // {225} with two non privileged planes which belong to two opposite families (one with $h>l$, the other with $h<l$) has also been studied in both materials. The structural unit model is still relevant in the sense that the units found in these ATGBs come from the units observed in the corresponding symmetric TGBs, although no predicitve algorithm is usable any longer. ATGBs stay relatively narrow in fcc metals, compared to corresponding STGBs whereas they get significantly thicker in germanium (silicon) where they dissociate locally to form microcrystals bounded by as much of $\Sigma=3$ {111} as possible. These differences may be ascribed to the difference between soft metallic bonding and rigid covalent bonding.

Grain boundary misorientation distribution study in nickel based alloy after thermomechanical processing

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One of dominant elements for defect structure of polycrystalline materials are grain boundaries. Recently a novel microstructure characteristic, namely grain boundary misorientation distribution (GBMD) has been introduced in order to describe an influence of grain boundaries on macroproperties and to control desired physico-mechanical behaviour by altering GBMD. In our previous investigations it was shown that GB spectrum in nichrome is quite stable and cannot be changed by heat treatment.

The aim of the present paper was finding of the heat treatment, which allows to design in the specimen a microstructure with highest fraction of special (CSL) grain boundaries. Ni-20%Cr alloy after recrystallization was deformed in tensile with 5% in total elongation at room temperature. Deformed samples were annealed were heated up to 850 °C, 900 °C, 950 °C and 1050 °C at heating rate of about 120 °C/min. From these temperatures the specimens were quenched into water.

Microstructure of the Ni-20%Cr samples obtained were investigated by means of optical and scanning electron microscopes and x-ray diffraction. The samples were polished and etched. Different etching methods allow revealing different types of grain boundaries. For quantitative analysis a total length of CSL and random grain boundaries were measured which being normalised by the total area gives relative length of the grain boundaries under study. Heating to the 950 °C leads to the microstructure of the Ni-20%Cr alloy with maximum length fraction of CSL boundaries of 80%. Measurements of GB statistics carried out by orientation imaging microscopy confirm these results.

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In-situ observation of grain rotations in an ultrafine-grained aluminum alloy

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Significant differences of the properties of nano- and submicrocrystalline (SMC) materials from the properties of coarse-grained materials are related to their specific structure, in particular, to a large extent and non-equilibrium character of grain boundaries (GBs).

Experimental observations have shown that annealing of as-prepared nano- and SMC materials results in a change of their properties. A considerable part of this change occurs on the initial stages of annealing when there is no significant grain growth. It is natural to assume that these changes are associated with the recovery process on GBs, which are the basic defects of the SMC materials.

The goal of the present work is to study the GB recovery process in an alloy with a submicrocrystalline structure.

For the investigation an aluminum alloy Al - 2.4% (at.) Cu - 16 (at.) Zr has been chosen. The SMC structure in this alloy has been obtained by severe plastic deformation. The specimens were deformed by shear under high quasi-hydrostatic pressure up to true logarithmic deformations $e = 7$. As a result, an SMC structure with the grain size in a range 0.15 to 0.25 μm was obtained. In a part of a thin foil taken from an as-prepared specimen the misorientations of several grain boundaries were determined. Then the specimen was annealed *in-situ* at T=433 K for 120 seconds and the evolution of the microstructure in the selected part of the specimen was observed. After the annealing the misorientations of the selected boundaries were measured again.

A single reflex method has been used to determine the misorientations of GBs. According to this method, an orientation matrix of each grain is determined first and on the basis of these matrixes a misorientation matrix of the GB is found. This method allows one to monitor the change of the orientation of each grain under study during the annealing process. For this, a misorientation matrix is determined between the initial position and the position after annealing for the same grain. The misorientation angles obtained have been interpreted as a grain rotation during the annealing. The grain rotation angles thus determined (up to 2.4°) are 3 to 4 times in excess of the maximum possible experimental error.

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Diffusion and softening of phase boundaries in superplastically deformed fine-grained eutectics

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Mechanical behaviour of phase boundaries, stability of defects and microstructure in the binary eutectics (Pb-Sn, Cd-Sn, Bi-Sn) heavily deformed by different schemes and regimes have been investigated. Experiments were carried out on the atomically–clean surfaces of alloys and on the bimetallic joints with clean interphases. Bimetallic joints obtained by special cold welding are used as a model analogue of deformed phase boundaries [1]. The results showed softening of phase boundaries when total deformation exceeded 30- 40 %. After deformation 50% the strength of phase boundaries falls very sharply. In this state phase boundaries demonstrated superplastic flow with m=0.7-1. This corresponds to increase of plasticity of the alloy and decrease of grain size to 0.5μm. It has been shown, that the plastic deformation on phase boundaries occurs by viscous flow and is accompanied by correlated diffusion of components along boundaries. The formation of pores, cracks or migration of phase boundaries in this case is not observed. It could be explained by intensive development of the correlated diffusion-promoted accommodation and dissolution-precipitation processes on phase boundaries. This causes the fast healing of defects. Intensity of softening and development of diffusion depend on phase boundary energy and the extent of preliminary deformation. After heavy deformation (total $\varepsilon > 100\%$) the phases of alloys are strengthened and relaxation processes occur mainly on the boundaries.

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Micromechanical properties and failure of AlN, TiN and AlN/TiN nanostructured multilayer coatings

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Coatings of AlN, TiN and nanostructured multilayer AlN/TiN have been deposited by reactive sputtering on sapphire, tungsten carbide (WC) and stainless steel substrates. The microhardness, adhesion, formation of cracks under indentation tests and the chemical composition by use SIMS method were investigated.

The obtained data for all investigated samples showed a non-uniform distribution of the microhardness inside the nitride coatings. Microhardness in the near–surface layer of 0.2-0.3 μm was by 25-60% higher than in the bulk of the coating. Such behaviour could be caused by a non-uniform stress distribution in the plasma coatings or formation of carbide on the surface.

The nanostructured multilayer AlN/TiN films were more plastic, showed a lower microhardness (≈20GPa) and heigher fracture toughness if compared to that for AlN and TiN "single layer" coatings (≈30 GPa). The principle of superposition fails to meet also in the adhesion tests of the multilayers. It was demonstrated that the nanostructured multilayer AlN/TiN films have the best adhesion and fracture toughness both on the hard (WC) and on the soft (stainless steel) substrates. Such behaviour may be related to the nanostructured state, for which the combination of high strength and sufficient plasticity is typical and which is favourable for comparatively intense relaxation processes on the interfaces.

It was found that the microhardness of nanostructured multilayer coatings depends on the bilayer thickness. The role of interfaces in the mechanisms of deformation and failure of multilayer coatings is discussed.

Influence of strong disorder on superconductivity of MgB_2

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Recently discovered superconductivity in MgB_2 raised questions about the origin and peculiarities of superconducting state in this compound. MgB_2 has a hexagonal crystal structure with boron layers separated by magnesium layers. For thin films deposition usually are preferable substrates, matching the crystal structure of the material. In the case of MgB_2 suitable substrates are sapphire or MgO. In this report we investigated the influence of disorder on superconductivity of MgB_2 films, prepared in single deposition run onto two different substrates: (100)-MgO, and (128^0 rot)-$LiNbO_3$ with trigonal crystal structure, not matching to MgB_2 structure. As expected, the microstructure of both films, prepared by two-step process of dc magnetron sputtering from Mg-MgB_2 composite target [1], crucially differs. REM study detected a very homogeneous, smooth morphology of the MgB_2 film, deposited onto MgO, but very rough inhomogeneous film structure on $LiNbO_3$. Specific resistance of the MgB_2 film on $LiNbO_3$, $\rho_n = 4.6 \cdot 10^{-4}$ Ohm·cm, is ~10 times higher than ρ_n for MgB_2 film of better quality on MgO substrate, also evidencing strong disorder of the film. In spite of strong disorder of the MgB_2 film on $LiNbO_3$, its critical temperature $T_c = 33.5K$ is the same as for the film deposited on MgO.

The possible reasons of such unusual T_c behavior are discussed.

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Driving forces for segregation analyzed in 12 fcc metallic systems at surfaces and grain boundaries (atomistic simulations)

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We have carried out extensive atomistic calculations to study the relative contributions of the three classically recognized driving forces for segregation, viz. the Gibbs excess energy, the (McLean) size energy and the alloy effect [1], in a coherent panel of four face centered cubic metals, nickel, copper, silver and gold so that twelve systems can be studied with a large variety of atomic size ratios and cohesive energy differences. We studied segregation in the infinite dilution limit at three surfaces, (110), (100) and (111) and in two symmetric tilt grain boundaries, the Σ=11 {113}<110> which has a low excess energy and a purely mirror-plane symmetric structure and the Σ=11 {332}<110> which has a high excess energy and a glide mirror plane symmetric structure. These two grain boundaries have stable atomic structures which have been experimentally confirmed by high resolution transmission electron microscopy on nickel [2]. We used a coherent set of Finnis-Sinclair like potentials. The stacking fault energy was explicitly included in the fitting data set for nickel and copper. Optimized configurations are obtained by viscous damping and quenched molecular dynamics. The size effect is analyzed along three lines, the Pines-Eshelby-Friedel-McLean elastic formula, the Kelires-Tersoff pressure work formula [3] and the Legrand's atomic size procedure [4]. Systematic conclusions can be drawn. Although the elastic formula gives the right order of magnitude, the last procedure is by far the most reliable. The size effect is always largely predominant when the solute atom is larger than the solvant atoms. Only for surfaces and for small solute atoms is the Gibbs site excess energy dominating. The alloy effect might be important only in the gold-silver systems for which there is no size effect. Pressure and Voronoï volume excess analysis proves useful to classify the atomic sites in grain boundaries.

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Distortion background and GB diffusion properties versus misorientation: comparative analysis

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Kinetic coefficients of thermally activated transport processes such as self-diffusion or diffusion of impurities in any condensed system with long range ordering are completely conditioned (at the absence of exterior electrical or magnetic fields and at the fixed temperature and pressure) by atomic scale structure of the system under consideration. Structural aspect of diffusion in bulk crystalline materials is distinct with that in quasi-two-dimensional systems such as interfaces in the following sense. The distinction may be most easily explained in the class of model crystalline and bicrystalline systems, which are generated by point particles (atoms) interacting with an appropriate pair interatomic potential.

Bulk crystal structures with the conditions of tight binding on the free surface, if it is vacancy-less, is not distorted at least sufficiently far from free surface. In contrast with crystalline systems any complete interfacial atomic configuration in a model bicrystalline system after relaxing procedure leaves to be distorted even if initial bicrystalline state was prepared as a vacancy-less one. This is the unremovable rest distortion what is intrinsically appropriate to any GB structure. Therefore one can to introduce in the situation the notion *of distortion background* what characterizes any stable GB configuration and what is absent in the limit of low concentration of vacancies in crystalline systems.

It has been discussed in the paper the contribution of the *distortion background* into kinetic coefficients such as a) mobility of a GB vacancy; b) mobility of a GB impurity ad-atom; c) GB diffusion coefficient. For the purpose GB distortion background for any misorientation is estimated quantitatively with the help of *mean-squere distortion* of elementary atomic tetrahedra belonging to GB. A comparative qualitative analysis of mean-square distortion versus GB misorientation and GB diffusion coefficient versus misorientation is carried out. It is shown that the relationships have identical positions of points of maxima and minima in the whole misorientation space.

Low-temperature limits of a) GB vacancy mobility, b) GB impurity ad-atom mobility and c) GB diffusion coefficient are considered. It is shown that due to the existence of GB distortion background the limits d) are non-zero ones; e) the limits depend on GB misorientation qualitatively in the same manner as GB mean-square distortion, i.e. points of maxima and minima of the limits versus misorientation are the same as points of maxima and minima of GB mean-square distortion versus misorientation. The behavior of GB diffusion coefficient for impurities in the limit of low concentrations of vacancies versus GB misorientation is analyzed to conclusion. One can expect that the limit is non-zero. Besides that one can expect that the limit may exhibit a dependence on GB misorientation by virtue of the existence of a strong dependence of GB atomic structure on misorientational parameters.

Internal friction in microcrystalline metals and alloys processed by ecap technology

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The experimental and theoretical investigations of internal friction in bulk microcrystalline metals and alloys: copper (99.98 wt.%), nickel (99.9 wt.%), chrome bronze (Cu - 0.4 wt.% Cr) and superplastic alloys of Al-[Zn]-Mg-Sc-Zr and Mg-[Al]-Zn-Zr were carried out. The materials studied had special microstructure with characteristic grain size 150 ÷ 400 nm. This structure was processed by equal channel angular pressing (ECAP) technology. (Dr. V.I. Kopylov produced the samples of microcrystalline materials.) The goal of research was to reveal the regularities of recovery and recrystallization processes in microcrystalline materials using acoustic techniques.

Internal friction were measured by the resonance acoustic technique at the frequency ~1 kHz and inverted torsion pendulum at the frequency ~1 Hz. The internal friction measurements were carried out during heating within the temperature range of 20 - 500 °C and isothermal annealing at the temperature range from 100 to 400 °C. The investigations have shown the internal friction in microcrystalline materials essentially differs from the internal friction values of coarse-grained metals at the same temperature range. The experimental study of microcrystalline metals and alloys has shown an existence of the recrystallization peaks and other anomalies on the temperature dependence of internal friction as compared to the coarse-grained metals.

The nonmonotonous behaviour of internal friction curves can be explained by the dislocation and grain-boundary models of internal friction taking into account the distinctive features of microcrystalline metal materials (small grain size, high dislocation density, nonequilibrium state of grain boundaries, intensive processes of recovery and recrystallization). The proposed internal friction models are effective for describing of internal friction in bulk microcrystalline materials produced by ECAP-technology.

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Prediction of interfacial segregation

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Systematic measurements of solute segregation at individual grain boundaries performed in the last decade, have brought an improved understanding of the phenomenon. It revealed a qualitatively similar orientation dependence of enthalpy of segregation of different elements that enables to construct grain boundary segregation diagrams. In addition, a linear dependence between the enthalpy and entropy of segregation of various solutes at individual grain boundaries of the same matrix was found. Based on these two fundamental findings, a method of prediction of the entropy and enthalpy of segregation of any element at any grain boundary was recently proposed. Based on the knowledge of the bulk phase diagram of a particular binary system only, the solute segregation in a wide spectrum of grain boundaries, segregants, bulk compositions and temperatures can be determined. This method will be presented and discussed, and its ability will be documented by comparing the prediction with literature data for numerous Fe–based binary systems.

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Electric activity of dislocation networks in plastically deformed silicon and germanium crystals

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The transmission electron microscopy images gave evidence to a cellular structure forming in Si and Ge crystals after plastic deformation up to shear stains of $\delta \sim$ 20-30 % at high temperatures. In heavily deformed samples most dislocations ($N_D = 10^9 - 10^{10}$ см$^{-2}$) are arranged in the walls of numerous cells 1-10 μm in size, the dislocations in the walls being connected in the form of various nets [1].

The distinct feature of plastically heavy deformed Ge crystals is an observation of the low temperature dc electric conductivity, which increases with δ and is attributable to motion of electrons or holes, captured by dislocations, along the connective system of dislocation segments. In the frame of modern theoretical conceptions the spatial-temporal evolution of dislocation systems is determined by a development of cooperative phenomena and dislocation self-organization in the process of plastic deformation of the crystals. The variation of external and internal parameters in the process of dislocation segment system formation leads to a change of the connectivity and the degree of ordering in dislocation structure. Influence of the strain rate and the high temperature annealing on the dislocation conductivity was investigated and these results are presented.

In contrast to Ge, the heavy plastic deformation of Si crystals at high temperatures does not promote observation of such dislocation conductivity as in Ge, despite of the similar dislocation structure. To clarify the reason of this difference dislocation photoluminescence in Si crystals (with various impurity contents) after the high temperature plastic deformation was investigated. These results are presented and allow us to explain, why the dislocation conductivity in Si crystals with dislocation networks is not observed.

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Mass transfer in Au-Ni system - from micro to nanoscale

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The generalized Darken method of interdiffusion (GDM) is presented. This method is based on the concept of separation of diffusional and drift flows. Its solution enables obtaining an exact expression for the evolution of component distributions for arbitrary initial distributions and time dependent boundary conditions. The existence and uniqueness of the solution of GDM [1-3] allows to formulate inverse problem of GDM [4]. Thus, it enables calculation of both constant and variable intrinsic diffusivities.

Diffusion studies were performed in the Au-Ni system at 700 and 750 ^{o}C. Computer simulations of the interdiffusion process in the Au-Ni system, in which intrinsic diffusivities of the components are functions of theirs composition, are presented. The type of a function which can be used to approximate the diffusivities is postulated.

The goal of the present paper is to show a great potential of the generalized Darken method of interdiffusion in describing the mass transport in thin layers. The evolution of the component distributions for different thickness of diffusional couple (0.5÷10 μm) is presented. The agreement between the calculated on the base of GDM and experimental profiles is observed both for the infinite and finite systems. Our results show the prospect for the GDM in the modelling of the diffusional mass transport in solids from micro to nanoscale.

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The model of diffusion at interface; the solution of initial boundary-value problem in R^3

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To model the diffusion in the vicinity of interphase (in multiphase material) we analyze the general situation of the non-steady diffusion in a bicrystal formed by two different crystalline phases (grains) having cubic geometry and different transport properties. The contact layer between the two media, the interphase, shows different diffusivity from the surrounding material. Through the "upper" surface of such bicrystal, the flow of mass occurs and the local concentration of mass on this surface is a known function of time and position. The initial distribution of the diffusing element is an arbitrary known function as well. We assume that except the "upper" surface, no other mass inflow into the bicrystal is allowed (the transport of mass does not occur through other boundaries). Finally we assume the Fick'ian diffusion and mass conservation at all interfaces. We have formulated the variational form of such problem. We present an exact analytical formula, method of its solution and an effective software that allows to find the distribution of the diffusing element. We will show the results of practical computation of nitrogen diffusion in multiphase alloys.

Structure and behavior of grain boundary film in ceramics

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Quantitative EELS analysis with high spatial resolution can be utilized in ceramic systems to obtain various information about grain boundary structure and composition, thanks to the distinct spectral features that allow separating the bonding contribution of the boundary from that of the matrix. This 3D methodology has been extremely useful in obtaining the true chemical composition of the ~1nm thick amorphous films covering grain boundaries in silicon nitrides, which otherwise could not be probed directly. Results revealed an equilibrium film composition corresponding to the previously found equilibrium thickness, an oxynitride grain boundary phase that does not exist in bulk form. Many dopants including calcia and rare-earth could not significantly change the oxynitride structure. In silicon carbides, a mono-layer of boron-carbon bonding configuration was found to be the most stable grain boundary structure. Silica- and alumina-based film did exist, but they could change dramatically by various factors thus the films in SiC are hardly equilibrium. In oxides such as TZP, again a mono-layer of silica-yttria was found at grain boundaries without amorphous film. It is concluded that there is an interfacial structural transition barrier at 1 mono-layer level of segregation at general boundaries in ceramics.

Interfaces in nanostructured thin films: structure, phase transitions, role in the deformation mechanisms

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Nanostructured thin films are of interest because of their remarkable characteristics. Despite a certain progress in the field of nanostructured thin films, many problems focusing on the fundamental understanding of behavior of systems in nanoscale and the measurement of their properties still remain unsolved, which so far has limited the applicability of nanostructured thin films. A significant amount of the atoms in nanostructured materials may be located at the grain boundaries, raising the interest in this problem. In the present study, the current topics related to the characterization of interfaces in nanostructured thin films, the phase transition at interfaces, the role of interfaces in the deformation mechanisms are review and refer to our recent results on BN and multicomponent (Ti,Cr)-(Al,Si)-(C,B,N) films.

Great role of crystallography in the c-BN nucleation mechanism was demonstrated. The formation of an initial sp^2-bonded BN layer provided the favorable boundary conditions for the heteroepitaxial nucleation of cubic phase. The atomic structure of an interface within the nanocrystalline cubic BN was shown to depend on the orientation relationship between adjacent c-BN grains and the boundary inclination. The grain boundaries consisted of twin boundaries when two grains were oriented close to the $[110]_{c-BN}$ zone axis and the boundary plane was parallel to the $\{111\}_{c-BN}$ close-packed planes of adjacent grains. However, a thin layer, 1-2 nm, of sp^2-bonded BN formed between the c-BN grains when the boundary plane inclined a few degrees from the $\{111\}_{c-BN}$ planes of adjacent grains. In the last case the sp^2-bonded BN precipitates are thought to reduce the grain boundary energy [1-2].

Evidence for the ordered structure of grain boundaries in nanostructured Ti-Si-B-N and Ti-Al-B-N films was showed [3-4]. Extra half planes and well-developed growth ledges were frequently seen on either side of the grain boundary. The amorphous phase formed as individual grains of several nm, rather than as a thin, intergranular amorphous layer of uniform thickness. Our observations contradict the conclusion by Gleiter et al. [5-7] that a nanocrystalline microstructure with random grain orientations contains ordered crystalline phase in the grain interiors connected by an amorphous, intergranular glue-like phase. The HRTEM technique appears to have a clear limit in its application for the characterization of nanostructured films with random grain orientation and a crystallite size of less than 1 nm. Note that no special features of interface structures that could be attributed to the small scale were seen in this study.

Multicomponent films was shown to posses either well-developed or latent columnar structure. As a result, the voids and low-density regions can surround the columns. It was suggested that the column sliding is the dominant fracture mechanism [8].

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Measuring the properties of triple junctions

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Triple junctions have been shown to exhibit real influences upon the behavior of polycrystalline materials, such as the exertion of a drag force retarding the migration of grain boundaries, and providing a location for excess segregation, beyond that which is observed at the adjacent grain boundaries. We provide a brief overview of current results on the effects that triple junctions exert upon materials.

The most fundamental property of a triple junction is its energy, and at least one paper has suggested that a triple junction may have "negative energy." In the present paper, we consider methods for measuring triple junction energy, and demonstrate what must be done in order to achieve this goal, *via* surface profilometry using an atomic force microscope. We estimate the change in surface profile that might be expected if triple junctions have realistic energies, and show that there is a strong effect of grain size (and therefore of grain size distribution) upon the results.

We also discuss the measurement of diffusion in triple junctions, presenting some new results from the copper-silver system.

Grain boundary dynamics in high magnetic filds

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The movement of grain boundaries is one of the fundamental mechanisms of microstructure evolution during heat treatment of metallic materials. Therefore, control of grain boundary motion means control of microstructure evolution, which is a key for the design of advanced materials. Grain boundary motion can be affected by a magnetic field, if the anisotropy of the magnetic susceptibility generates a gradient of the magnetic free energy. In contrast to curvature driven boundary motion, a magnetic driving force also acts on flat boundaries so that the motion of crystallographically fully defined boundaries can be investigated, and the true grain boundary mobility can be determined. By appropriate positioning and repositioning of the specimen in the magnetic field the energy gradient can be changed and even inverted for the same boundary. This allows for the first time to study asymmetry effects of boundary dynamics. We will report in detail results obtained on Bi and Zn bicrystals. Selective grain growth in deformed Zn monocrystals and texture changes in Zn alloy sheet in high magnetic filds will be discussed.

Local characterization of discontinuous precipitation in a Cu-4.5 at.% In alloy

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The discontinuous precipitation reaction has been studied in a Cu-4.5 at.% In alloy by means of analytical electron microscopy. Before the precipitation at the grain boundary starts, a movement this grain boundary was experimentally observed. Subsequently, the typical lamellar two-phase microstructure for the discontinuous precipitation reaction has developed, where the phase involved are the In-depleted solid solution (α) and the intermetallic phase Cu_7In_3 (δ). Indium concentration profiles were determined in the wake of the moving reaction front and parallel to it for individual α lamellae by application of energy-dispersive X-ray microanalysis. A local analysis was applied to describe the kinetics of this reaction and the local grain-boundary diffusivity was determined.

Grain boundary “wetting” (covering) by solid phase in the Fe–C system

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